Reaction of Diazoalkanes with 4-Substituted 1,2,4-Triazole-3,5(4*H*)-diones[1]

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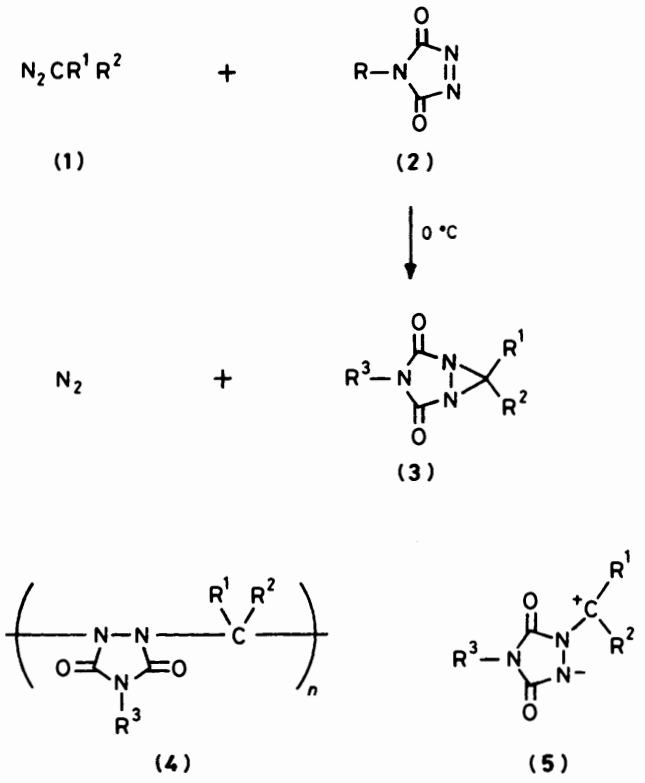
Diazoacetic esters reacted with 4-substituted 1,2,4-triazole-3,5(4*H*)-diones (**2**) to give one-to-one adducts. Molecular weight determination, high-performance liquid chromatography, and 2D n.m.r. spectroscopy showed that the adducts are monomers that associate in solution. The monomers are most likely 1,3,5-triazabicyclo[3.1.0]hexane-2,4-diones. The adducts were thermally isomerized to 3,6-disubstituted 1,3,5-triazine-2,4(1*H*,3*H*)-diones. Diphenyldiazomethane reacted with (**2**) to yield an azomethine imine, which underwent thermal dimerization followed by rearrangement.

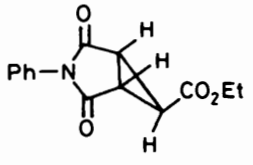
Diazoalkanes were reported in earlier literature to react with *trans*-diacyl diamides to give diaziridines.[2–5] It was later shown that the products from these reactions are actually oxadiazolines,[6] hydrazones,[7–9] or semicarbazones.[10,11] A number of years ago we presented evidence of the first example of an addition reaction of an alkyl diazoacetate to a *cis*-diacyl diimide. Ethyl diazoacetate (**1a**) was found to react with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (**2a**) in dichloromethane or benzene at 0 °C, with nitrogen evolution, to yield a one-to-one adduct, which was identified as ethyl 2,4-dioxo-3-phenyl-1,3,5-triazabicyclo[3.1.0]hexane-6-carboxylate (**3a**) (Scheme 1).[12] Compound (**3a**) was stable to both aqueous hydrochloric acid and acetic acid, and very unstable to aqueous sodium hydroxide. It underwent a double nucleophilic displacement reaction with sodium acetate or lead diacetate in the presence of acetic acid to give 4-phenyl-1,2,4-triazolidine-3,5-dione. Since the time of our initial publication, a number of papers concerned with reactions between diazoalkanes and 1,2,4-triazole-3,5(4*H*)-diones have been published.[13–20] α-Acyldiazoalkanes were reported to yield triazole oligomers (**4**) rather than monomeric bicyclic diaziridines (**3**).[13–16,19] The assignment of the oligomeric structure (**4**) was based on molecular weight data obtained by vapour-phase osmometry and ebullioscopic methods. The product from (**1a**) and (**2a**), for example, was determined to be a trimer of type (**4**) (R^1 = CO_2Et, R^2 = H, R^3 = Ph).[13] Another group of authors reported this same product to be a tetramer but did not assign a structure.[19] Several studies have shown that α-aryldiazoalkanes form azomethine imines (**5**).[8,14–18,21] Compounds (**5**) were characterized by their high dipole moments and high u.v. molar absorptivity values, and their ability to give 1,3-dipolar cycloadducts with dimethyl acetylenedicarboxylate and phenyl isocyanate.[14–16,18,21] In this report we describe the results of our further investigation of the reaction between (**1**) and (**2**).



Scheme 1. For R, R^1, R^2, and R^3 see Table 1

Results and Discussion

Reactions of diazoalkanes (**1**) and 4-substituted 1,2,4-triazole-3,5(4*H*)-diones (**2**) were performed as described previously.[12] The reactants, products, and yields of the isolated products are summarized in Table 1. The ^{1}H n.m.r. spectra of the alkoxycarbonyl-substituted products (**3b**—**e**) were similar to those observed for (**3a**) in that the alkoxycarbonyl and aromatic protons were recorded as broad and unresolved multiplets.[12] The proton-decoupled ^{13}C n.m.r. signals (25.2 MHz) were also considerably broadened. Decoupling of the methyl and methylene signals, respectively, of (**3a**) by double resonance did not markedly effect the shapes of the peaks of the nonirradiated protons. The occurrence of 'slow' dynamic processes in molecules can lead to a broadening of their n.m.r. signals.[22] These processes can generally be detected by the use of variable-temperature n.m.r. spectroscopy. The ^{1}H and ^{13}C n.m.r. signals of the methyl ester (**3b**) were as severely broadened as those of the ethyl esters (**3a**) and (**3c**—**e**), and no change in the ^{1}H n.m.r. spectrum of (**3a**) was observed as the temperature was varied between −78 and 110 °C. In contrast the ^{1}H n.m.r. signals of the bicyclic compound (**6**) were found to be sharp and fully resolved. In (**6**) both slow inversion at nitrogen and slow rotation about the C–C=O bond might be expected. It is



(**6**)

Table 1. Products isolated from the reaction of diazoalkanes with 4-substituted 1,2,4-triazole-3,5(4*H*)-diones

Diazoalkane (**1**)	Triazoledione (**2**)	Product	Yield (%)
a; $R^1 = CO_2Et$, $R^2 = H$	**a**; R = Ph	(**3a**; $R^1 = CO_2Et$, $R^2 = H$, $R^3 = Ph$)	98
b; $R^1 = CO_2Me$, $R^2 = H$	**a**	(**3b**; $R^1 = CO_2Me$, $R^2 = H$, $R^3 = Ph$)	93
a	**b**; R = 4-ClC_6H_4	(**3c**; $R^1 = CO_2Et$, $R^2 = H$, $R^3 = 4\text{-}ClC_6H_4$)	95
a	**c**; R = 4-$MeOC_6H_4$	(**3d**; $R^1 = CO_2Et$, $R^2 = H$, $R^3 = 4\text{-}MeOC_6H_4$)	90
a	**d**; R = 4-BuC_6H_4	(**3e**; $R^1 = CO_2Et$, $R^2 = H$, $R^3 = 4\text{-}BuC_6H_4$)	90
c; $R^1 = R^2 = Ph$	**a**	(**5a**; $R^1 = R^2 = R^3 = Ph$)	98

Table 2. Molecular weight determinations for (**3b**)

Method	*M*
Mass spectrometry	247
Vapour-phase osmometry	2 470[a]
Freezing-point depression	245,[b] 336[c]

[a] Solvent chloroform at 37 °C. [b] Determined in camphor. [c] Determined in 2,4,6-tribromophenol.

evident that neither slow rotation nor slow inversion is responsible for the broadening of the n.m.r. signals of compounds (**3**). A 10^{-3}M-solution of (**3a**) in chloroform did not give an e.s.r. spectrum. Therefore, the broadened n.m.r. signals were not caused by the presence of a paramagnetic species in solution.

Broadened n.m.r. signals are often characteristic of polymeric species. Compounds (**3**) are white amorphous solids that could not be converted into crystals, and it was not possible to determine by *X*-ray crystallography whether the isolated compounds were monomers or polymers. Therefore, less direct methods were employed. The molecular weight of (**3b**) was determined under a variety of conditions (Table 2). The mass spectrum gave a molecular ion at *m/z* 247 and was void of peaks at higher masses.* The molecular weight obtained for (**3b**) in solution was directly proportional to the temperature at which the experiment was carried out. In chloroform at 37 °C the molecular weight corresponded to a decamer of (**3b**). In 2,4,6-tribromophenol and in camphor at the respective melting points, the molecular weights were near that of monomeric (**3b**); the value determined in the higher-melting solvent, camphor, was within experimental error (±5%) of the theoretical value. The results are consistent with the occurrence of an equilibrium process in solution involving monomers and associated forms of (**3b**). At lower temperatures the equilibria favour the associated forms, and at sufficiently high temperatures they favour the monomeric form: (**3b**) $\rightleftharpoons$ $(\mathbf{3b})_n$ ($n \geqslant 2$).

Solutions of (**3a**) in acetonitrile were analysed by reverse-phase high-performance liquid chromatography (h.p.l.c.) on an octadecylsilane column. A solvent program with acetonitrile–water (70:30) for minutes 0—7 and changing by linear gradient to pure acetonitrile during minutes 7—10 was employed. The appearance of the chromatograms varied with the concentration of the solution of (**3a**). Relatively dilute solutions gave a pattern of overlapping peaks at t_R 1.0—3.0 min. Relatively concentrated solutions gave additional peaks. At concentrations near saturation a complex pattern of peaks extending from t_R 1.0—6.5 min and a broad high-intensity peak at t_R 10—16 min were obtained. The long-retention-time peak corresponded to the major component at high concentrations of (**3a**). It diminished in intensity and corresponded to the minor component as the concentration was lowered, and it disappeared at relatively low concentrations. The long-retention-time component was isolated by preparative h.p.l.c. Its m.p. behaviour and i.r. and ^{1}H n.m.r. spectra were unchanged from those of nonchromatographed (**3a**). When the component was rechromatographed (h.p.l.c.) it gave only short-retention-time peaks in dilute solution and both short- and long-retention-time peaks in concentrated solution; this behaviour was identical with that observed before. Solutions of (**3c**) were analysed under the same h.p.l.c. conditions, and similar results were obtained. The h.p.l.c. results are in agreement with a process involving the reversible association of compounds (**3**) in solution, with the extent of association directly proportional to the concentration of the solution.

Solutions of (**3a**) and (**3c**) in deuteriochloroform were analysed by homoscalar *J*-resolved two-dimensional (2D) ^{1}H n.m.r. spectroscopy at 400 MHz. At a concentration of 120 mg ml^{-1} the contour diagram of compound (**3a**) showed ten fully resolved triplets and three partially resolved triplets at δ_H 1—1.4. Ten singlets appeared at δ_H 3.5—4.0, and four fully resolved and two partially resolved quartets appeared at δ_H 4.2—4.5. The aromatic region gave a pattern of multiplets extending from δ_H 7.1 to 7.9. The various singlets and multiplets had various intensities. The methyl, methylene, and methine regions of the *J*-resolved 2D ^{1}H n.m.r. spectrum are illustrated in Figure 1. The methine hydrogen singlets of (**3a**) clearly appear upfield from those of the methylene hydrogens. We previously did not observe this signal as a separate peak in the 100 MHz ^{1}H n.m.r. spectrum.[12] When the solution of (**3a**) was diluted, the number of singlets and multiplets in the various regions decreased and the signals appeared over narrower chemical shift ranges. When the concentration of (**3a**) was increased to near saturation (250 mg ml^{-1}), the number of peaks in the F2 (p.p.m.) dimension increased and the signals appeared over a wider chemical shift range; the peaks overlapped in the high peak-density regions of the spectrum. Compound (**3c**) gave *J*-resolved 2D ^{1}H n.m.r. spectra similar to those of (**3a**). Attempts to record heteroscalar *J*-resolved ^{13}C, ^{1}H and heteroscalar *J*-correlated ^{13}C, ^{1}H 2D n.m.r. spectra of (**3a**) and (**3c**) were not successful. This difficulty was probably caused by the low concentration of the individual species in solution, even though the overall concentrations of (**3**) were relatively high. It is not clear as to what types of species are represented by the individual peaks in each region of the homoscalar *J*-resolved 2D ^{1}H n.m.r. spectra. Indeed, the exact number of peaks in each region at a given concentration may not have been accurately determined. It is possible that a higher peak resolution than that available at 400 MHz or a higher number of data acquisitions would lead to a higher number of peaks. However, the observed correlation between the complexity of the spectra with the concentration of the sample in each case agrees well with the h.p.l.c. results already discussed and is consistent with a process involving a reversible association of products (**3**) in solution. The presence of the relatively high number of resolved singlets and multiplets and

* The mass spectra of (**3a** and **b**) gave low intensity peaks at *m/z* 322. This mass corresponds to that of the molecular ion of (**13a**) probably formed by partial decomposition of (**3a** and **b**) at the high temperatures (170—180 °C) used to introduce the samples into the mass spectrometer. No other peaks were observed above the masses of the molecular ions.

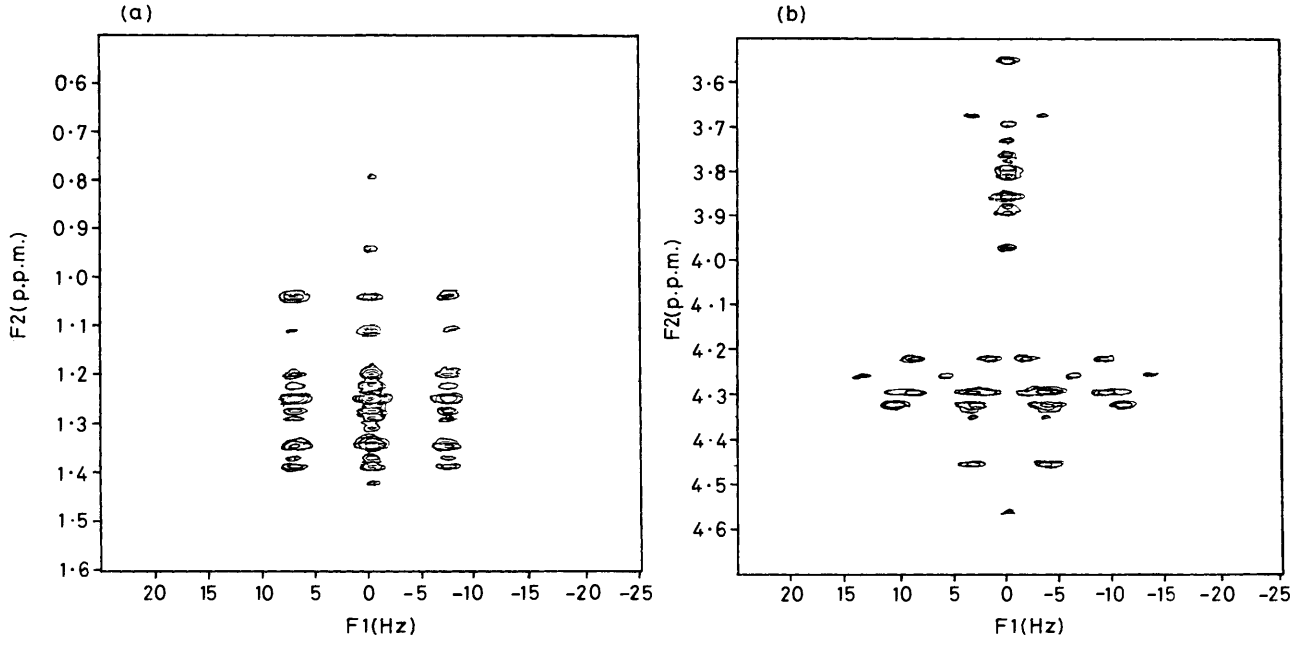
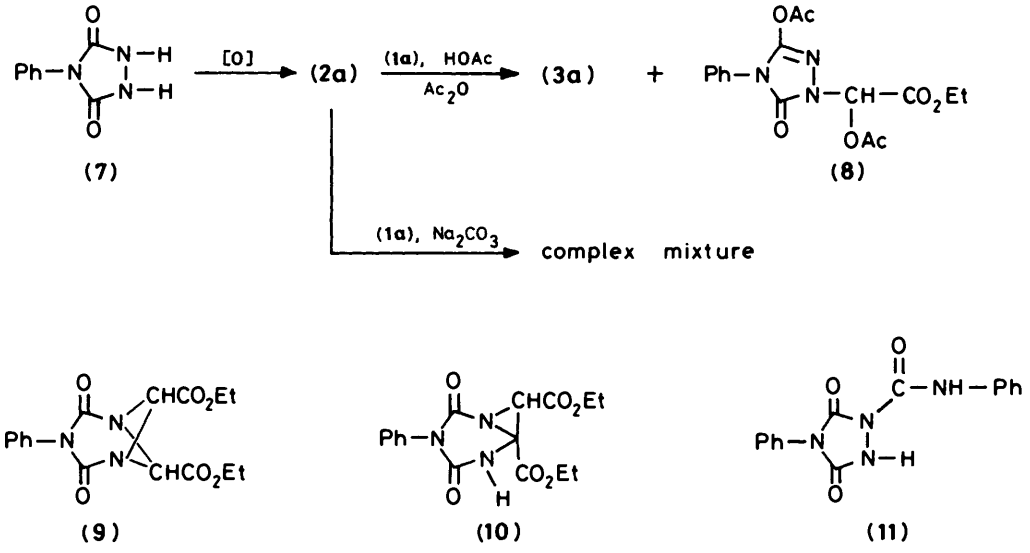


Figure 1. (a) Methyl and (b) methylene and methine regions of the *J*-resolved 2D ^{1}H n.m.r. spectrum of compound (**3a**)



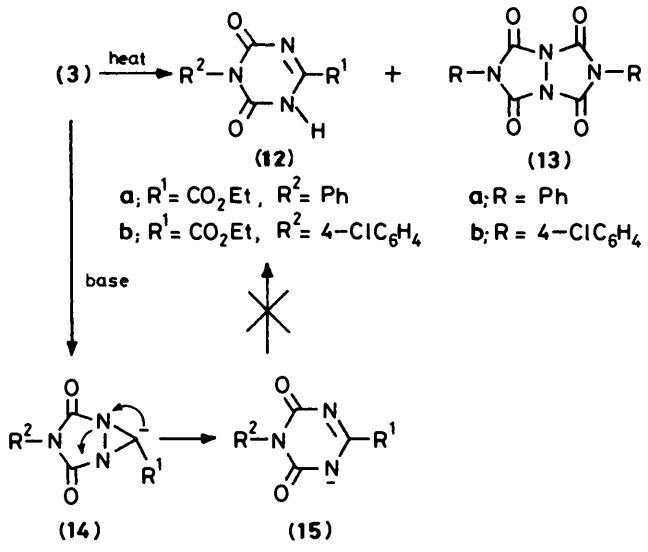
Scheme 2.

their varying intensities rule out simple oligomeric forms (**4**) as the structures of the compounds.

The proton-decoupled 1D ^{13}C n.m.r. spectra of (**3a**) and (**3c**) were recorded at 100.5 MHz. The broad peaks obtained at 25.2 MHz were resolved at the higher field into numerous closely spaced singlets in each region. Each compound exhibited its ethoxy signals near δ_C 14 and 64. The methine carbon signals were not clearly observed as a separate set of peaks. They are probably included in the set of methylene carbon peaks at δ_C 64; this would be analogous to the close proximity of the methylene and methine signals in the ^{1}H n.m.r. spectra.

Diphenyldiazomethane (**1c**) reacted with (**2a**) to yield the azomethine imine (**5a**) as a bright red-orange solid. The structure of (**5a**) was assigned on the basis of spectral data. The compound was reported previously.[16,17] The visible spectrum of (**5a**) showed $\lambda_{max.}$(EtOAc) 431 nm (ε 8 000). The high value of the molar absorptivity is characteristic of ylides similar to (**5a**).[23–25] The azomethine imine (**5a**) is unstable to atmospheric moisture, decomposing to 4-phenyl-1,2,4-triazolidine-3,5-dione and benzophenone. It must be stored in a vacuum desiccator or under an inert atmosphere.

Several attempts were made to trap (**2a**) *in situ* in order to avoid the need for its isolation *via* sublimation. It was also of interest to develop a trapping procedure for future use with other cyclic *cis*-diacyl di-imide systems. Most of the known *cis*-diacyl di-imides are not nearly as stable as the 1,2,4-triazole-3,5(4*H*)-diones, and they must be generated (usually by oxidation of a hydrazide precursor) and trapped in solution at low temperatures.[26–32] Reported methods for oxidizing the hydrazides generally lead to acidic media. It was necessary to use trapping conditions that were neither too acidic, to prevent decomposition of (**1**), nor too basic, to prevent decomposition of the products (**3**). We reported in our original communication that the *in situ* reaction of (**2a**), prepared by oxidation, with lead



Scheme 3.

tetra-acetate, of 4-phenyl-1,2,4-triazolidine-3,5-dione (**7**), gave a relatively low yield (30—40%) of (**3a**) plus a small quantity (1—3%) of the ring-opened product (**8**) (Scheme 2). In the present study compound (**2a**) was prepared in dichloromethane at 0 °C by oxidation of (**7**) with t-butyl hypochlorite. Sodium carbonate and sodium sulphate were added as neutralizing and drying agents, respectively, followed by (**1a**). Complex mixtures of water-soluble, acidic, and neutral water-insoluble components were isolated. The desired compound (**3a**) was not observed. The acidic mixture of components showed *m/z* 347 and 296 in its mass spectrum. These two masses are consistent with the presence of (**9**) or (**10**) and (**11**), but the products were not isolated as pure compounds. The latter compound (**11**) is a decomposition product of (**2a**).[33] The other components were not identified. It is likely that (**3a**) was formed initially, but was unstable under the relatively mild basic reaction conditions because of the presence of the acidic hydrogen on the three-membered ring. When (**1c**) and (**2a**) were allowed to react under the conditions of this trapping procedure, the azomethine imine (**5a**) was isolated in high yield (88%).

In our previous communication we reported that heating (**3a**) at 150 °C and 10 Pa gave a mixture containing the 1,3,5-triazine-2,4(1*H*,3*H*)-dione (**12a**) and the triazolo[1,2-*a*]triazole (**13a**) (Scheme 3). The presence of (**13a**), which is a primary thermal decomposition product of (**2a**),[33] suggested that ethoxycarbonylcarbene and (**2a**) were produced as thermolysis products. The structure of (**12a**) was assigned on the basis of its mass spectrum, which showed *m/z* 261, and its ^{1}H n.m.r. spectrum, which showed resolved splitting patterns for the ethoxy signals. However, (**12a**) was not isolated as a pure compound. In the present study (**3a** and **c**) were converted into derivatives (**12a** and **b**) by heating in refluxing chlorobenzene. The reaction was followed by monitoring the precipitation of (**13a** and **b**), which ceased after 14 days. The products (**12a** and **b**) were purified by recrystallization followed by preparative t.l.c. on silica gel. They are hygroscopic and readily solvated. It was necessary to heat (**12a** and **b**) under vacuum to drive off the purification solvents in order to obtain samples suitable for analysis. The i.r. spectra of both products gave N–H absorptions at 3 300—3 440 cm^{-1} and carbonyl absorptions from 1 740 to 1 760 cm^{-1}. The ^{1}H n.m.r. spectra showed sharp, well resolved ethoxy multiplets as well as the aromatic hydrogen signals.

The structure of compound (**12b**) was analysed by *X*-ray

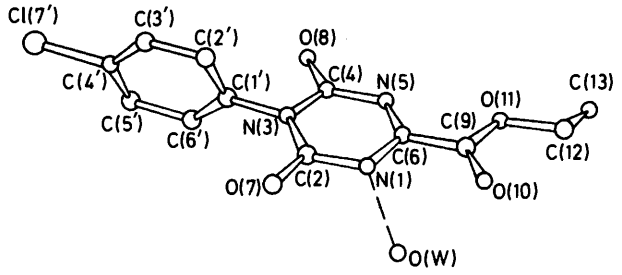
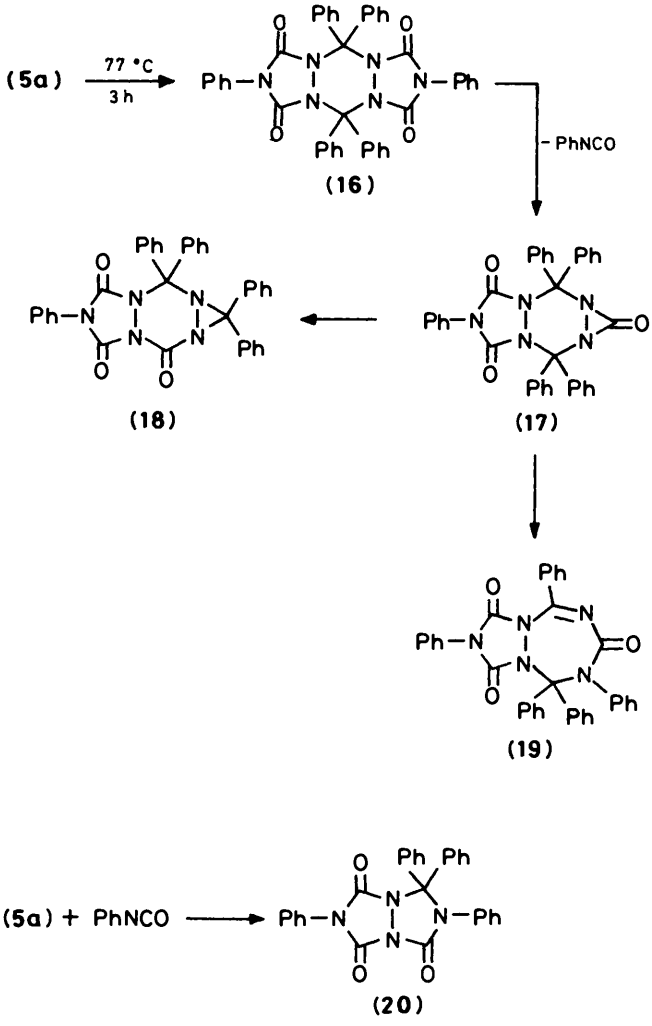


Figure 2. ORTEP drawing of compound (**12b**); the water molecule is located at postion 1

crystallography (by direct methods using the MULTAN 76 suite of programs). The data showed that the crystals contained a water molecule of crystallization at position 1 of the ring (Figure 2). The acidic hydrogen is located on the ring nitrogen rather than on the oxygen of its hydroxy imine tautomer. The water in the *X*-ray sample was probably absorbed from atmospheric moisture, as the crystals were formed by evaporating a solution of (**12b**) in acetone in the atmosphere. The water molecules are an integral part of the crystal structure. They probably serve to link molecules in the crystal by hydrogen bonding.

Attempts were made to isomerize (**3a**) to (**12a**) *via* the anions (**14a**) and (**15a**). A solution of (**3a**) in dichloromethane was stirred over sodium carbonate to produce a complex mixture of acidic products, as shown by analysis by h.p.l.c. Compound (**12a**) was not detected; this result is analogous to those obtained in the trapping experiment.

The azomethine imine (**5a**) was thermally unstable in solution at room temperature. The rates of decomposition were monitored by visible spectroscopy by observing the rates of decrease in the molar absorptivities at $\lambda_{max.}$. In this manner 10^{-4}M-solutions of (**5a**) were found to undergo 50% decomposition during 3 h in dry chloroform and during 8 h in dry ethyl acetate. The thermal decomposition of (**5a**) in refluxing ethyl acetate exposed to air in one experiment and kept under nitrogen in another experiment was complete after 3 h to give the same products in each instance. No gas evolution was observed. A white, ether-insoluble solid was isolated and identified as the triazolo[1,2-*a*]triazole (**20**). A white ether-soluble solid was also isolated, which showed $\nu_{max.}$ 1 762 cm^{-1} (C=O) and *m/z* 563, and gave analytical figures consistent with $C_{35}H_{25}N_5O_3$. Structures (**17**)—(**19**) are consistent with the mass spectrometric molecular ion and with elemental analysis data. Structure (**17**) can be ruled out on the basis of the i.r. spectrum and the previously demonstrated thermal instability of *cis*-diaziridinones.[34] The diaziridinone carbonyl absorption of (**17**) is expected to be observed at 1 855—1 880 cm^{-1}.[34,35] The mass spectrum gave a base peak at *m/z* 341, which would result from losses of phenyl isocyanate and benzonitrile molecules, respectively, from the molecular ion. These two losses are more likely to occur from the molecular ion of (**19**) than from that of (**18**). Therefore, the ether-soluble compound is tentatively identified as (**19**). These results are in disagreement with a previous report that the dimer (**16**) was isolated in quantitative yield when (**5a**) was heated in refluxing benzene for 2—3.5 h.[17] The identification of (**16**) was based on i.r. spectroscopy and elemental analysis data. The m.p. (219—221 °C) and i.r. and elemental analysis data of the reported compound, which was insoluble in hexane–ether, are very near to those of our ether-insoluble product (**20**), m.p. 224—225 °C. It is suggested that the reported compound is actually (**20**) rather than (**16**). A proposed mechanism for the decomposition reaction is given in Scheme 4. The initially formed intermediate

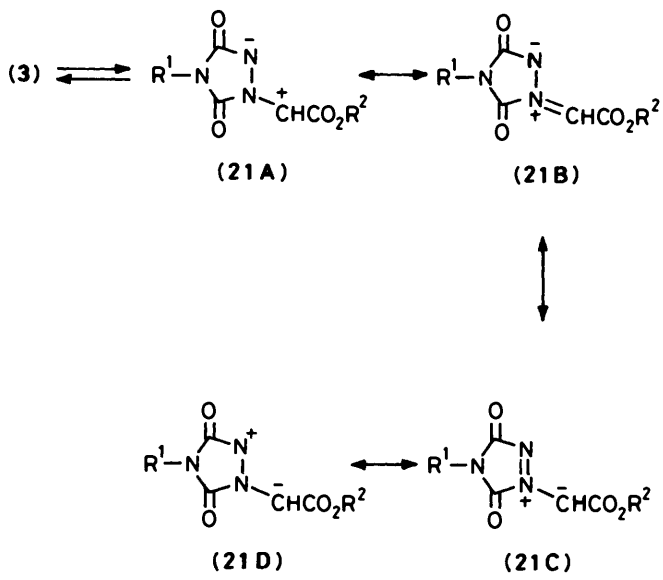


Scheme 4.

(16) loses phenyl isocyanate to produce (17), which then undergoes rearrangement to give either (18) or (19). The phenyl isocyanate is trapped by (5a) to yield (20).

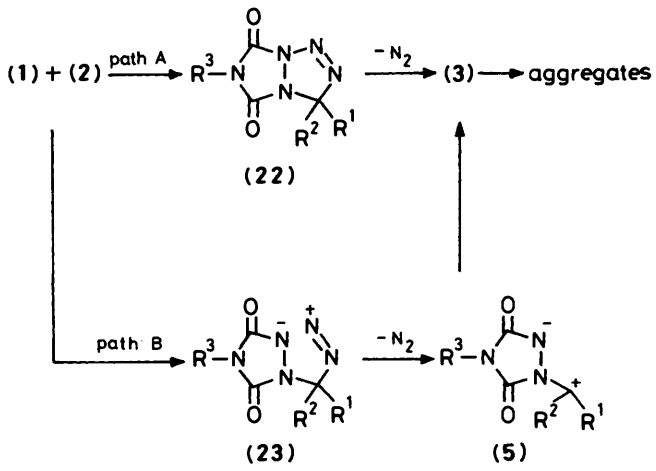
The reactivity of the bicyclic compounds (3) with 1,3-dipole trapping agents was investigated to determine if the dipolar forms (21A—D) could be trapped. Compound (3a) was recovered unchanged after it was heated with an equimolar quantity of dimethyl acetylenedicarboxylate in refluxing benzene for 3 h or in refluxing acetone [36] for 3 h. This behaviour differs from that of the stable azomethine imines (5), which react readily as 1,3-dipoles.[14–18,21] These latter molecules have stabilizing aromatic groups on the positively charged carbon. None of the reported adducts from (2) and diazoacetic esters or α-diazo ketones have been shown to react with 1,3-dipolarophiles. The failure of the 6-alkoxycarbonyl derivatives of (3) to behave as 1,3-dipoles is perhaps not surprising. Each of the two 1,3-dipolar forms (21A and D) contains a destabilized positive charge. These two forms are not expected to conribute significantly to the resonance hybrid, and therefore reactivity as a 1,3-dipole is prevented.

The results of the molecular weight, h.p.l.c., and 2D n.m.r. studies performed on the products obtained from (1) and (2) show convincingly that the products are monomers that associate in solution. The extent of the association is dependent on the nature of the solvent and on the concentration and the temperature of the solution. The products are not simple



oligomers. There are a number of possible explanations of the association in solution. In order for an explanation to be viable, it should account for the chemical properties of the products, namely their stability to acid, instability to weak bases, reactivity with nucleophiles, thermal conversion into triazines (12), and nonreactivity as 1,3-dipoles. The explanation should also be consistent with the spectral and other physical properties of the products and provide a mechanism for the reversible association that occurs in solution. On the basis of these criteria, it is possible that the products are (i) monomeric bicyclic diaziridines that aggregate in solution; (ii) polymeric in the usual sense; (iii) polymers that readily dissociate in solution into monomeric units; (iv) azomethine imines that aggregate in solution; or (v) monomeric bicyclic diaziridines that aggregate in the form of dipoles.

It is reasonable to assume that the nonassociated forms of the products are responsible for the observed chemical reactivity. On the basis of this assumption, it can be concluded that the observed chemical properties are consistent with those expected for the monomeric bicyclic diaziridines (3) and inconsistent with those expected for polymers or dipoles (5). Thus explanations (ii) and (iv) can be ruled out. The type of dissociation of polymers stated in explanation (iii) is expected to have a high energy requirement and is not commonly observed. This explanation is viable only if the polymers dissociate into monomeric (3), but the dissociation, if it occurred, most likely would give (5) instead of (3). Explanation (iii) is probably not correct. Explanations (i) and (v) can both account for the properties of the products. However, explanation (i) does not offer an obvious mechanism for the aggregation. Explanation (v) does not have this drawback. The aggregates of (v) can arise through intermolecular dipole–dipole attractions. The dipoles, in the instances of the 6-alkoxycarbonyl-substituted derivatives of (13), can be ascribed structures of type (21C). Forms (21A, B, and D) can be eliminated from consideration because the products do not react as 1,3-dipoles and no vinyl hydrogen signals were observed in the ^{1}H n.m.r. spectra. It is not obvious how (3) can be converted directly and reversibly into aggregates of (5) without the intermediacy of monomeric (5). However, monomeric (5) is expected to be unstable to acid, contrary to observation. Explanation (i) must remain as a viable explanation. It was found, for example, that in the case of the reaction between (1; $R^1 = R^2 = H$) and (2a) that the product showed a far greater measured degree of association than any product obtained either with electron-donating or with electron-



Scheme 5.

withdrawing groups on the α-diazo carbon.[15] At present then the explanation for the aggregation of products (3) is not clearly understood, but explanations (i) and (v) remain as viable alternatives.

The presence of only two groups of ethoxy signals in the ^{13}C n.m.r. spectra of (3a and c) might be taken as evidence that one isomer, presumably the *exo*-isomer, was preferentially formed in each instance. However, because the spectra were recorded for aggregates, which may not contain bicyclic diaziridine units, and a high number of singlets were present in each of the two groups, no definite conclusion on this matter can be drawn.

Depicted in Scheme 5 are two mechanistic pathways for the formation of products (3) from (1) and (2). Path A involves a concerted 1,3-dipolar cycloaddition followed by loss of nitrogen. Path B corresponds to a stepwise addition to give (3) through intermediates (23) and (5). The formation of (22) along path A is a symmetry-allowed process. It is analogous to the 1,3-dipolar cycloadditions of (1) to carbon–carbon double bonds conjugated to carbonyl groups, which occur readily below room temperature to give pyrazolines.[37,38] Path B leads to unstable intermediates (5) in those cases in which R^1 or R^2 is an electron-withdrawing group. Intermediates (5) have been reportedly trapped with alcohols to give triazolinediones.[14,18–20] However, path B is not required for the formation of these products, which can arise through ring-opening of the diaziridine ring of (3) by the nucleophilic alcohols, analogous to the formation of (8) from (3a) in acetic acid. Moreover, the failure of (3) to react with dipolarophiles argues against the formation of (5) as an intermediate. Reaction along path A is consistent with the experimental observations, and it appears to be more favourable than reaction along path B. The stable azomethine imines (5) that are obtained from (2) and α-aryldiazoalkanes can arise from ring opening of initially formed (3), and need not arise from reaction along path B.

Experimental

M.p.s were determined on a Mel-Temp apparatus. I.r. spectra were recorded with a Beckman Acculab 10 spectrophotometer. U.v.–visible spectra were obtained with a Beckman DBG spectrophotometer. N.m.r. spectra were recorded with Varian EM-360A, XL-100, and XL-400 spectrometers. Tetramethylsilane was used as an internal reference for the ^1H and ^{13}C n.m.r. spectra. Homoscalar *J*-resolved ^1H n.m.r. spectra were recorded with a Varian XL-400 spectrometer using the HOM2DJ pulse sequence. Mass spectra were determined with an AEI-902 mass spectrometer at the Research Triangle Institute of Mass Spectrometry, Research Triangle Park, North Carolina. The *X*-ray crystallographic structure determination of compound (12b) was performed by Professor Andrew T. McPhail at Duke University, Durham, North Carolina.* High-performance liquid chromatography (h.p.l.c.) data were obtained with a Varian 5020 or a Waters Associates liquid chromatography system. Vapour-phase osmometry measurements were made by Galbraith Laboratories, Knoxville, Tennessee. Elemental analyses were performed by Integral Microanalytical Laboratories, Raleigh, North Carolina.

The 4-substituted 1,2,4-triazolo-3,5(4*H*)-diones (2) were prepared by the stepwise procedure of Cookson, Gupte, Stevens, and Watts.[39] Methyl diazoacetate (1b) was synthesized by the procedure of Searle.[40] Diphenyldiazomethane was prepared as described by Smith and Howard.[41] t-Butyl hypochlorite was prepared using the method of Teeter and Bell.[42] Ethyl diazoacetate was purchased commercially.

General Procedure for the Reaction of Diazoalkanes (1) with 1,2,4-*Triazole*-3,5(4H)-*diones* (2).—To a solution of the 1,2,4-triazoline-3,5(4*H*)-dione (20 mmol) in dichloromethane (200 ml) at 0 °C, the diazoalkane (1) (20 mmol) was added dropwise over 10 min with stirring. Stirring was continued until the red colour of (2) had faded (1—3 h). The solution was filtered and evaporated to dryness under reduced pressure. The resulting solid was purified by recrystallization, by (i) dissolving it in hot tetrachloromethane–chloroform (1:1), (ii) cooling the solution to room temperature, and (iii) adding light petroleum (b.p. 40—60 °C) or hexane dropwise with swirling to precipitate (3), with the following properties.

Aggregates of ethyl 2,4-*dioxo*-3-*phenyl*-1,3,5-*triazabicyclo*-[3.1.0]*hexane*-6-*carboxylate* (3a); m.p. 175—177 °C (decomp.) [Found: C, 55.3; H, 4.1; N, 16.0; M^+ (70 eV), 261. $C_{12}H_{11}N_3O_4$ requires C, 55.2; H, 4.25; N, 16.1%; *M*, 261]; $\nu_{max.}$(Nujol) 1 745 cm^{-1} (CO); δ_H(400 MHz; $CDCl_3$) 1.3 (3 H, br m, CH_3), 3.8 (1 H, br s, CH), 4.3 (2 H, br m, OCH_2), and 7.5 (5 H, m, Ph); δ_C(100.5 MHz; $CDCl_3$; ^1H-decoupled) 13.0—14.5 (overlapping s, CH_3), 62.0—65.5 (overlapping s, OCH_2 and CH), 124.5—127.5 and 128.0—131.5 (overlapping s, Ph), and 152.8—165.0 (br overlapping s, CO).

Aggregates of methyl 2,4-*dioxo*-3-*phenyl*-1,3,5-*triazabicyclo*-[3.1.0]*hexane*-6-*carboxylate* (3b); m.p. 176—177 °C (decomp.) [Found: C, 53.1; H, 3.8; N, 16.85; M^+ (70 eV), 247. $C_{11}H_9N_3O_4$ requires C, 53.4; H, 3.6; N, 17.0%; *M*, 247]; $\nu_{max.}$(Nujol) 1 740 cm^{-1} (CO); δ_H(100 MHz; $CDCl_3$) 3.75 (1 H, br s, CH), 3.88 (3 H, br m, OMe), and 7.45 (5 H, m, Ph); δ_C(25.2 MHz) 54.0 (br, OMe and CH), and 123—126 and 128—131 (br, overlapping s, Ph); *M* (vapour-phase osmometry; $CHCl_3$; 37 °C) 2 470; *M* (freezing-point depression; camphor), 245; *M* (freezing-point depression; 2,4,6-tribromophenol), 336.

Aggregates of ethyl 3-(4-*chlorophenyl*)-2,4-*dioxo*-1,3,5-*triazabicyclo*[3.1.0]*hexane*-6-*carboxylate* (3c); m.p. 174—176 °C (decomp.) [Found: C, 48.6; H, 3.4; N, 14.0; M^+ (70 eV), 295.0362. $C_{12}H_{10}N_3O_4$ requires C, 48.75; H, 3.4; N, 14.2%; *M*, 295.0360]; $\nu_{max.}$(Nujol) 1 740 cm^{-1} (CO); δ_H(400 MHz; $CDCl_3$) 1.3 (3 H, br m, CH_3), 4.25 (1 H, br m, CH), 4.35 (2 H, br m, OCH_2), and 7.5 (4 H, m, 4-ClC_6H_4); δ_C(100.5 MHz; $CDCl_3$; ^1H-decoupled) 13.0—14.5 (overlapping s, CH_3), 62.0—65.5 (overlapping s, CH and OCH_2), 120.8—131.8 and 133.2—137.5 (overlapping s, 4-ClC_6H_4), and 148.0—166.0 (br overlapping s, CO).

Aggregates of ethyl 3-(4-*methoxyphenyl*)-2,4-*dioxo*-1,3,5-*triazabicyclo*[3.1.0]*hexane*-6-*carboxylate* (3d); m.p. 175—178 °C

* Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see section 5.6.3 of Instructions for Authors, in the January issue).

(decomp.) (Found: C, 53.65; H, 4.7; N, 14.4. $C_{13}H_{13}N_3O_5$ requires C, 53.6; H, 4.5; N, 14.4%); $\nu_{max.}$(Nujol) 1 740 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 1.3 (3 H, br m, CH_2CH_3), 3.7 (3 H, br m, OMe), 4.3 (3 H, br m, CH and OCH_2), and 6.4—7.6 (4 H, m, 4-$MeOC_6H_4$).

Aggregates of ethyl 3-butyl-2,4-dioxo-1,3,5-triazabicyclo-[3.1.0]*hexane-6-carboxylate* (**3e**); m.p. 94—96 °C (decomp.) (Found: C, 49.6; H, 6.4; N, 17.1. $C_{10}H_{15}N_3O_4$ requires C, 49.8; H, 6.3; N, 17.4%); $\nu_{max.}$(Nujol) 1 740 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 0.6—1.9 (10 H, br m, $CH_3[CH_2]_2$ and CH_3CH_2O), 3.5 (2 H, br m, CH_2N), and 4.2 (2 H, br m, OCH_2).

2-Diphenylmethyliumyl-3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-ide (**5a**).—To a solution of the 1,2,4-triazole-3,5(4*H*)-dione (**2a**) (0.95 g, 5.4 mmol) in dry ethyl acetate (50 ml) at 0 °C a solution of diphenyldiazomethane (1.05 g, 5.4 mmol) in dry ethyl acetate (10 ml) was added dropwise over 10 min with stirring. After 2 h the solid was removed by filtration and washed with ethyl acetate to yield the ylide (**5a**) as red-orange crystals. The product was dried and stored in a vacuum desiccator. The synthesis of (**5a**) was also carried out by trapping (**2a**) [formed *in situ* by the oxidation of (**8**; R = Ph) with t-butyl hypochlorite in dry ethyl acetate at 0 °C in the presence of an excess of sodium carbonate and anhydrous sodium sulphate] with (**1c**). The salts were removed by filtration prior to the addition of (**1c**). The trapping procedure gave an 88% yield of (**5a**); m.p. 229—232 °C (decomp.) (lit.,[8] 126—133 °C) (Found: C, 74.0; H, 4.35; N, 12.25. Calc. for $C_{21}H_{15}N_3O_2$: C, 73.9; H, 4.4; N, 12.3%); $\lambda_{max.}$(EtOAc) 431 nm (ε 8 000); $\nu_{max.}$(Nujol) 1 710 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 7.4 (m, aromatic CH); *m/z* (70 eV) 341 (M^+, 22%) and 119 (100).

General Procedure for the Synthesis of the Alkyl 5-Aryl-1,4,5,6-tetrahydro-4,6-dioxo-1,3,5-triazine-2-carboxylates (**12**).—A solution of the bicyclic diaziridine (**3**) (20 mmol) in chlorobenzene (250 ml) was heated at reflux for 2 weeks. The mixture was cooled to room temperature, and the precipitate was removed by filtration. The filtered solid was stirred in dichloromethane (200 ml) for 30 min and filtered to remove the triazolo[1,2-*a*]triazole-1,3,5,7-tetraone (**13**) (25—35%). The dichloromethane solution was evaporated to dryness under reduced pressure to give the crude triazine (**12**). Purification was accomplished by recrystallization from chloroform–cyclohexane or chloroform–light petroleum (b.p. 40—60 °C). If necessary the recrystallized (**12**) was further purified by preparative t.l.c. on silica gel. It was necessary to heat the purified (**12**) under vacuum to drive off the purification solvents.

Ethyl 1,4,5,6-tetrahydro-4,6-dioxo-5-phenyl-1,3,5-triazine-2-carboxylate (**12a**) (18.0%) had m.p. 168—170 °C (decomp.) [Found: C, 55.05; H, 4.2; N, 16.5; M^+ (70 eV), 261.0747. $C_{12}H_{11}N_3O_4$ requires C, 55.2; H, 4.3; N, 16.1%; M^+, 261.0749]; $\nu_{max.}$(Nujol) 3 440 (NH), 1 746 (CO), 1 779 (CO), and 1 607 cm^{-1} (CN); $\lambda_{max.}$(MeOH) 257 nm (ε 3 700); δ_H[60 MHz; $(CD_3)_2CO$] 1.37 (3 H, t, CH_3), 4.39 (2 H, q, OCH_2), and 7.31 (5 H, m, Ph).

Ethyl 3-(4-chlorophenyl)-1,4,5,6-tetrahydro-4,6-dioxo-1,3,5-triazine-2-carboxylate (**12b**) (21.4%) had m.p. 214—215 °C (decomp.) [Found: C, 48.65; H, 3.3; N, 14.0; M^+ (70 eV), 295.0362. $C_{12}H_{10}ClN_3O_4$ requires C, 48.7; H, 3.4; N, 14.2%; *M*, 295.0360]; $\nu_{max.}$(Nujol) 3 430 (NH), 1 759 (CO), 1 740 (CO), 1 666 (CO), and 1 590 cm^{-1} (CN); $\lambda_{max.}$(MeOH) 260 nm (ε 3 900); δ_H[60 MHz; $(CD_3)_2CO$] 1.39 (3 H, t, CH_3), 4.38 (2 H, q, OCH_2), 4.8 (1 H, br s, NH), and 7.37 (4 H, m, 4-ClC_6H_4).

Thermal Decomposition of the Ylide (**5a**).—A solution of the ylide (**5a**) (2.05 g, 6 mmol) in dry ethyl acetate (150 ml) was heated at reflux under N_2 for 3 h, during which the colour of the solution changed from deep red to pale yellow. Evaporation under reduced pressure left a gummy residue, which was stirred in dry diethyl ether for 1 h. The mixture was filtered to remove *6,7-dihydro-2,6,7,7-tetraphenyl*[1,2,4]*triazolo*[1,2-*a*][1,2,4]*triazole-1,3,5-trione* (**20**) as a white solid (0.90 g, 98%), m.p. 224—225 °C [Found: C, 72.85; H, 4.4; N, 12.3; M^+ (70 eV), 460. $C_{28}H_{20}N_4O_3$ requires C, 73.0; H, 4.4; N, 12.7%; *M*, 460]; $\nu_{max.}$(Nujol) 1 732 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 7.0—7.7 (m, aromatic CH). The ethereal solution was evaporated under reduced pressure to give *5,6-dihydro-2,5,5,6,9-pentaphenyl-*[1,2,4]*triazolo*[1,2-*a*][1,2,4,5]*tetrazepine-1,3,7-trione* (**19**) (1.1 g, 65%), m.p. 237—238 °C [from CCl_4–$CHCl_3$–light petroleum (b.p. 40—60 °C)] [Found: C, 74.8; H, 4.7; N, 12.2; M^+ (70 eV), 563. $C_{35}H_{25}N_5O_3$ requires C, 74.6; H, 4.5; N, 12.4%; *M*, 563]; $\nu_{max.}$(Nujol) 1 762 (CO) and 755 and 687 cm^{-1} (aromatic CH). When the decomposition reaction was carried out without a nitrogen atmosphere, no gas evolution was observed, and (**19**) and (**20**) were again isolated as the only two products.

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