The analytical sample was prepared by two recrystallizations from ether–heptane; mp 61–62 °C.

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.50; H, 6.14; N, 4.02.

Method C. To a suspension of 0.375 g (7.8 mmol) of a 50% mineral oil dispersion of NaH (prewashed with pentane) and 15 mL of dry *N,N*-dimethylformamide in 55 mL of CH_2Cl_2 was added over 3.5 h a solution containing 2.98 g (7.1 mmol) of **53** and 15 mL of dry *N,N*-dimethylformamide in 55 mL of CH_2Cl_2. After completion of the addition, the reaction mixture was stirred for 3 h at room temperature and then quenched with 10 mL of a saturated ammonium chloride solution. The resulting mixture was diluted with ether and CH_2Cl_2. The organic phase was separated, washed with water and with saturated aqueous sodium chloride, and then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave an orange oil which was crystallized from ether–hexane to give 1.9 g (80%) of white solid, mp 52–54 °C.

Diethyl α-[p-(Benzyloxy)phenyl]-2-oxo-1-azetidinemalonate (54). To a stirred solution of 0.33 g (2.0 mmol) of hexamethyldisilazane in 20 mL of dry tetrahydrofuran was added dropwise at −78 °C under nitrogen atmosphere 0.92 mL (2.0 mmol) of 2.2 M *n*-butyllithium in hexane. The solution was warmed to 0 °C for 15 min, cooled to −78 °C, and treated dropwise with 574 mg (1.7 mmol) of β-lactam **11** in 5 mL of tetrahydrofuran. After 2 h, the reaction mixture was treated dropwise with 0.22 g (2.0 mmol) of ethyl chloroformate, stirred for 2 h at room temperature, and quenched with 1 mL of saturated sodium chloride solution. Removal of the solvent under reduced pressure gave an oily residue which was dissolved in 100 mL of methylene chloride–ether (2:1) and washed successively with 1 N hydrochloric acid, 5% sodium bicarbonate solution, and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated to give 710 mg of yellow oil. Preparative layer chromatography over silica gel (hexane–ether, 1:1) gave 443 mg (64%) of malonate **54** as a colorless oil: IR (neat) 1740 (split), 1610, 1510 cm^{-1}; NMR ($CDCl_3$, 270 MHz) δ 7.40 (m, 5 H), 7.33 (d, J = 8.8 Hz, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 5.06 (s, 2 H), 4.33 (q, J = 7.0 Hz, 4 H), 3.47 (t, J = 4.4 Hz, 2 H), 2.95 (t, J = 4.4 Hz, 2 H), 1.30 (t, J = 7.0 Hz, 6 H); high-resolution mass spectrum, calcd for $C_{23}H_{25}NO_6$ m/e 411.1674, found m/e 411.1687.

Diethyl 3-Azido-α-[p-(benzyloxy)phenyl]-2-oxo-1-azetidinemalonate (55). To a stirred solution of 107 mg (1.1 mmol) of diisopropylamine in 20 mL of dry tetrahydrofuran at −78 °C under nitrogen atmosphere was added dropwise 0.5 mL of a 2.2 M solution of *n*-butyllithium in hexane. The solution was warmed to 0 °C for 15 min, cooled to −78 °C, and treated dropwise with 196 mg (0.48 mmol) of malonate **54** in 3 mL of tetrahydrofuran. After 2 h, 114 mg (0.58 mmol) of *p*-toluenesulfonylazide[12] was added in 2 mL of tetrahydrofuran, and stirring was continued for 2 h. The reaction was then treated dropwise with 265 mg (2.4 mmol) of trimethylchlorosilane and warmed to room temperature for 1 h. Removal of the solvent under reduced pressure gave an oily residue which was dissolved in 50 mL of methylene chloride–ether (2:1) and washed successively with 5% sodium bicarbonate solution and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated to give 126 mg of yellow oil. Preparative layer chromatography with 5% ethyl acetate–benzene gave 105 mg (48%) of azide **55**: IR (neat 2130, 1775, 1750, 1610, 1510, 1450, 1375, 1275 cm^{-1}; NMR ($CDCl_3$, 270 MHz) δ 7.37 (m, 5 H), 7.30 (d, J = 8.0 Hz, 2 H), 6.97 (d, J = 8.9 Hz, 2 H), 5.05 (s, 2 H), 4.57 (dd, J = 5.2, 2.6 Hz, 1 H), 4.32 (q, J = 7.0 Hz, 4 H), 3.78 (dd, J = 6.4, 5.2 Hz, 1 H), 3.36 (dd, J = 6.4, 2.6 Hz, 1 H), 1.29 (t, J = 7.0 Hz, 6 H).

Benzyl 3-Azido-α-[p-(benzyloxy)phenyl]-2-oxo-1-azetidineacetate (43 and 44). To a stirred solution of 31.0 mg (0.07 mmol) of azide malonate **55** in 0.5 mL of absolute methanol at 0 °C was added dropwise 0.14 mL (0.14 mmol) of 1 N sodium hydroxide solution. After completion of the addition, the reaction mixture was stirred at room temperature for 1 h and then neutralized with 0.14 mL (0.14 mmol) of 1 N hydrochloric acid. The solvent was then removed under reduced pressure, and the residue was chromatographed over silica gel with ethyl acetate elution to give 20.0 mg of yellow oil. Thin-layer chromatographic analysis of this material showed a 1:1 mixture of two products (R_f 0.63 and 0.41, 2% acetic acid–ethyl acetate) which compared identically with an athentic sample of a diastereomeric mixture of 3-azido-α-[*p*-(benzyloxy)phenyl]-2-oxo-azetidineacetic acid (**42**). To a suspension of azide acids **42** in 2.5 mL of dry acetonitrile was added 9.1 mg (0.09 mmol) of triethylamine followed by 15 mg (0.09 mmol) of benzyl bromide. After the mixture was heated at reflux for 6 h, the solvent was removed under reduced pressure, and the residue was chromatographed over silica gel (PLC, 0.25-mm layer) with 25% ethyl acetate–benzene. Recovery of the major band (R_f 0.56) gave 6.0 mg of azide benzyl esters **43** and **44** as a 1:1 mixture of diastereomers in 23% overall yield from **55**.

Acknowledgment. This work was supported by Grant GM-07874 from the National Institutes of Health.

Registry No. (±)-**4**, 68682-19-9; (±)-**11**, 77629-81-3; (±)-**12**, 68641-19-0; (±)-**14**, 77698-53-4; (±)-**15**, 43189-27-1; (±)-**15** hydrotosylate salt, 77629-82-4; **16**, 14062-18-1; (±)-**17**, 77629-83-5; (±)-**18**, 77629-84-6; (±)-**20**, 77629-85-7; (±)-**21**, 77629-86-8; (±)-**22**, 77629-87-9; (±)-**23**, 77629-88-0; (±)-**24**, 72028-75-2; (±)-**25**, 6324-01-2; (±)-**26**, 77629-89-1; (±)-**27**, 77629-90-4; **32**, 68641-16-7; **33**, 68641-17-8; **34**, 68641-18-9; **35**, 68641-20-3; **37**, 68641-21-4; **38**, 68641-22-5; **39**, 68641-23-6; **40**, 68641-24-7; (±)-**42** (isomer 1), 68641-25-8; (±)-**42** (isomer 2), 68641-26-9; (±)-**43**, 68682-16-6; (±)-**44**, 68682-17-7; (±)-**45**, 68682-21-3; (±)-**46**, 77629-92-6; (±)-**47**, 6324-01-2; (±)-**48**, 43189-09-9; (±)-**49**, 77629-93-7; (±)-**50** (isomer 1), 77629-94-8; (±)-**50** (isomer 2), 77629-95-9; (±)-**51**, 77629-96-0; (±)-**53**, 77629-97-1; **54**, 71725-07-0; **55**, 77629-98-2; 3-bromopropionyl chloride, 15486-96-1; cyclopropanone, 5009-27-8; ethyl chloroformate, 541-41-3.

2,4-Bis(arylimino)-1,3,5-triarylhexahydro-*s*-triazinones

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2,4-Bis(arylimino)-1,3,5-triarylhexahydro-*s*-triazinones (**7**) have been synthesized by several routes: (A) addition of phosgene to 2,4-bis(arylimino)-1,3-diaryl-1,3-diazetidines (**2**) leads to ring opening, giving *N*-(chloroimidoyl)-*N'*-(chlorocarbonyl)guanidines (**9**), which are readily cyclized to **7** with arylamine; (B) heating of N^1,N^2,N^3,N^4,N^5-pentaarylbiguanides (**10**) or N^1,N^2,N^3-triarylguanidines with diphenyl carbonate to 200–210 °C or reacting **10** with phosgene in the presence of triethylamine produces the diimino-*s*-triazinones **7** in good yield.

Aryl isocyanates and *N,N'*-diarylcarbodiimides are each known to cyclodimerize or trimerize in a head to tail fashion under certain conditions to afford either the 1,3-diazetidine derivatives **1** and **2** or the hexahydro-*s*-triazines

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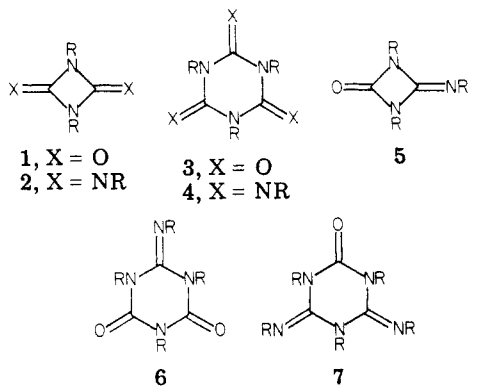
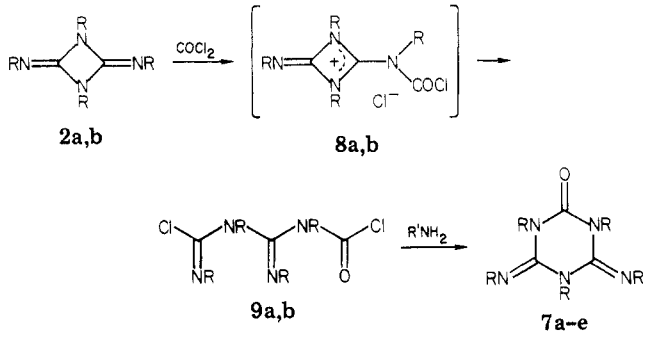
Chart I[a]



[a] R = aryl.

Scheme I

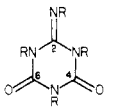
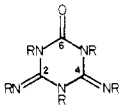


3 and 4[1-3] (Chart I). Cycloaddition reactions between both heterocumulenes afford only the thermolabile (2 + 2) adducts 5,[4] a class of compounds which is also accessible by other synthetic routes.[5] The six-membered ring cycloadducts 6, formally derived from two molecules of isocyanate and one molecule of carbodiimide, have also been prepared, although not by cotrimerization.[6] These compounds can be readily prepared either from *N,N*-bis(chlorocarbonyl)arylamine and N^1,N^2,N^3-triarylguanidines or from 2-(arylimino)-1,3-diaryl-1,3-diazetidinones (5) and aryl isocyanate in an HCl-catalyzed ring expansion.[7]

The 2,4-bis(arylimino)-1,3,5-triarylhexahydro-*s*-triazinones (7), formally cotrimers formed from two molecules of *N,N'*-diarylcarbodiimide and one molecule aryl isocyanate, have not been described to date. Knowledge about compounds of this type was important to us in connection with certain polymerization reactions of difunctional starting materials (diisocyanates, isocyanatocarbodiimides). In these cases, formation of only small amounts of heterocycles of type 7 could cause significant changes in polymer properties. We now describe the preparation and properties of 2,4-diimino-*s*-triazinones as derivatives of monofunctional heterocumulenes.

From 2,4-Bis(arylimino)-1,3-diaryl-1,3-diazetidines. 2,4-Bis(arylimino)-1,3-diaryl-1,3-diazetidines (2), the cyclodimers of *N,N'*-diarylcarbodiimides, contain a four-atom chain consisting of two imino group nitrogen units which we tried to utilize for the synthesis of 7. It was hoped that the four-membered ring could be opened with a carbonic acid derivative such as phosgene, which could extend the chain by one carbon atom. Treatment of **2a** (R = C_6H_5) in chloroform solution with excess phosgene led to formation of a pale yellow, moisture-sensitive solid which we believed to be the acyclic 1:1 adduct **9** (Scheme I), formed after initial attack of $COCl_2$ on one of the semicyclic C=N bonds. Samples of the reaction solution show the gradual appearance and disappearance of an IR band at 1660 cm^{-1} which coincides with the appearance of new bands at 1700 and 1740 cm^{-1}. These spectroscopic changes could be evidence for the formation of an intermediate of type 8. Attempts to purify the *N*-(chloroimidoyl)-*N'*-(chlorocarbonyl)guanidine (**9a**) failed due to partial decomposition (hydrolysis) during recrystallization which is indicated by intensity changes of the IR bands in the double bond region. The suspensions of **9a** were, after removal of excess phosgene, treated with aromatic amines to produce the expected triazine derivatives **7a–c** in good yield. The *N,N'*-di-*p*-tolylcarbodiimide dimer **2b** (R = C_6H_4-*p*-CH_3) yields the triazines **7d,e** in similar reactions. In these cases, however, the analogous chlorocarbonyl intermediate **9b** remains dissolved during the reaction.

Table I. ^{13}C NMR Shifts (ppm) of C-2, C-4, and C-6 of 6a,b and 7a,b ($CDCl_3/Me_4Si$)

compd type	no.	R	C-2(4)	C-4(6)
	**6a**	C_6H_5	137.96	*a*
	6b	C_6H_4-*p*-CH_3	138.18	149.70
	**7a**	C_6H_5	139.26	150.24
	7b	C_6H_4-*p*-CH_3	139.77	150.51

[a] Not detected; sample dissolved in CD_3CN/Me_4Si.

The novel perarylated diiminotriazinones 7 are highly crystalline, high-melting solids which show a characteristic pair of often unresolved IR bands in the double bond region at 1635–1640 and 1660 cm^{-1}. The shape and intensity of these double bands are very similar to those found in the spectra of the related (arylimino)-*s*-triazinediones 6. A ^{13}C NMR comparison of chemical shifts of imino carbons and carbonyl carbons in the rings of **6a,b** and **7a,b** (Table I) shows only small differences. The signals for the carbonyl carbons appear at approximately 150 ppm and those of the imino carbons at 138–140 ppm (in CD_3CN or $CDCl_3$) downfield from Me_4Si. The yields and melting points of the new compounds are given in Table II.

We tried to extend the synthetic principle of opening of an imino-1,3-diazetidine ring with phosgene to aryl isocyanate–*N,N'*-diarylcarbodiimide adducts of type 5. It was hoped that this reaction would lead to N^1,N^2-bis(chlorocarbonyl)-N^1,N^2,N^3-triarylguanidines, which are potentially useful for the synthesis of 2-(arylimino)-4,5-dioxohexahydro-*s*-triazines of type 6. When **5a** (R = C_6H_5) was reacted with phosgene, ring opening of the molecule was accompanied by fragmentation: phenyl isocyanate and N^1-(chlorocarbonyl)-N^1,N^2-diphenylchloroformamidine (adduct of carbodiimide and phosgene)[8] were obtained instead of N^1,N^2-bis(chlorocarbonyl)-N^1,N^2,N^3-triphenylguanidine.

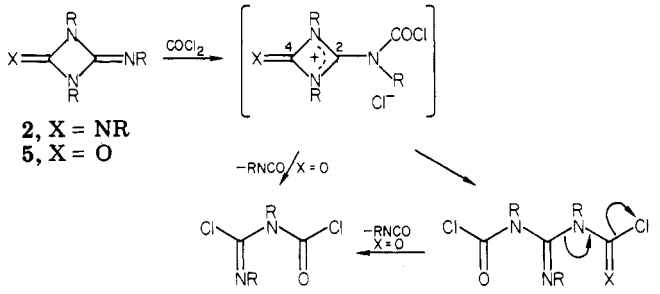
(1) For a review on oligomerizations of isocyanates see: Richter, R.; Ulrich, H. In "The Chemistry of Cyanates and Their Thio Derivatives"; Patai, S., Ed.; Wiley: Chichester, England, 1977; pp 667–678.
(2) Richter, R. *Chem. Ber.* **1968**, *101*, 174.
(3) Busch, M.; Blume, G; Pungs, E., *J. Prakt. Chem.* **1909**, *79* (2), 513.
(4) Farrissey, W. J., Jr.; Ricciardi, R. J.; Sayigh, A. A. R. *J. Org. Chem.* **1968**, *33*, 1913.
(5) Michler, W.; Keller, E. *Chem. Ber.* **1881**, *14*, 2181.
(6) Richter, R.; Ulrich, H. *Tetrahedron Lett.* **1974**, 1875.
(7) Formation of compounds of type 7 (R = aryl) has also been observed by: Gavin, D. F.; Schnabel, W. J.; Kober, E.; Robinson, M. A. *J. Org. Chem.* **1967**, *32*, 2511.
(8) Ulrich, H.; Sayigh, A. A. R., *J. Org. Chem.* **1963**, *28*, 1427.

Table II. 2,4-Bis(arylimino)-1,3,5-triarylhexahydro-s-triazin-6-ones (7)[a]

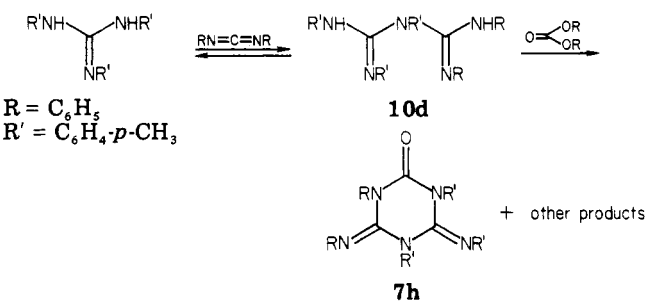
	R	R'	yield, % A[b]	B[b]	C[b]	mp, °C
7a	C_6H_5	C_6H_5	65(55)[c]	87	75	210–212
b	C_6H_5	C_6H_4-*m*-CH_3		80		182–183
c	C_6H_5	C_6H_4-*p*-CH_3		75		175
d	C_6H_4-*p*-CH_3	C_6H_5		78		189–190
e	C_6H_4-*p*-CH_3	C_6H_4-*m*-CH_3		65		155–156
f	C_6H_4-*p*-CH_3	C_6H_4-*p*-CH_3	66		73	195–196
g	C_6H_4-*p*-OCH_3	C_6H_4-*p*-OCH_3	54		50	193–194

[a] All values for the elemental analyses (C, H, N) were within ±0.3%. [b] Method A: from N^1,N^2,N^3,N^4,N^5-pentaarylbiguanide and diphenyl carbonate. Method B: from 2-(arylimino)-1,3-diaryldiazetidin-4-ones, phosgene, and arylamine. Method C: from N^1,N^2,N^3-triarylguanidine and diphenyl carbonate. [c] From **10a** and phosgene/triethylamine.

Scheme II



Scheme III

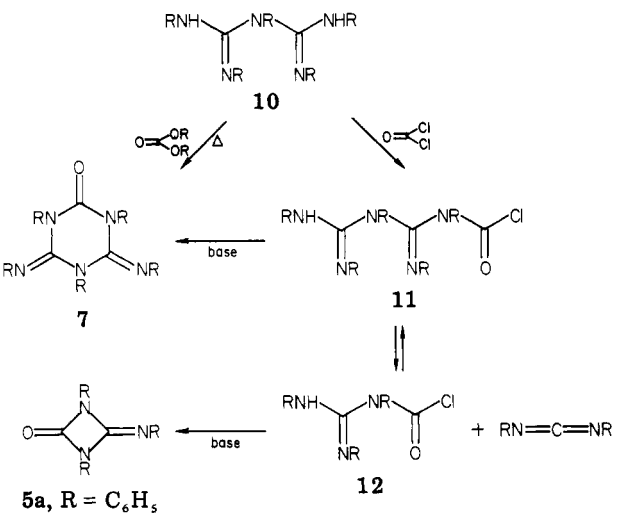


This marked difference in the ring opening of **2** and **5** during the phosgene addition is likely to be due to basicity differences of the ring nitrogens in the two rings: acylation of the 2-imino nitrogen in **5** by phosgene is followed by deacylation (isocyanate elimination) at N-1 (or N-3) of the ring. Such a deacylation is not observed with **2**. Deacylation can take place simultaneously with the ring opening by chloride addition at C-2 (followed by 1,2-bond breaking) or after formation of a linear intermediate, which is preceded by chloride addition at C-4 as shown in Scheme II.

From Pentaarylbiguanides and Carbonic Acid Derivatives. 2,4-Bis(arylimino)-1,3,5-triarylhexahydro-*s*-triazin-6-ones of type **7** are also formed in moderate yield on brief heating of equimolar mixtures of N^1,N^2,N^3,N^4,N^5-pentaarylbiguanides **10a–c** and diphenyl carbonate to 200–210 °C. After cooling, the glassy melts are treated with small amounts of methanol, which leads to separation of the *s*-triazines in crystalline form and in high purity. No reactions take place if the reactants are heated in refluxing chloroform for a prolonged period of time. Yields and IR spectroscopic data of the *s*-triazines obtained by this method are given in Table II. The pentaarylbiguanides required for these cyclizations are easily prepared in virtually quantitative yield on treatment of *N,N'*-diarylcarbodiimides with 0.5 mol of the corresponding arylamine at room temperature. The addition reactions, which give N^1,N^2,N^3-triarylguanidines in the first step, are complete within 1 h (followed by disappearance of the IR band of the carbodiimide at 2140 cm^{-1}).

When a biguanide with differing aryl substituents is heated with diphenyl carbonate, a mixture of triazines is obtained. It is known that guanidines and biguanides dissociate and recombine on heating, which will cause scrambling of N-substituents and consequently lead to a mixture of heterocyclic products in the condensation with diphenyl carbonate. Thus, heating of the biguanide **10d**, derived from N^1,N^2,N^3-tri-*p*-tolylguanidine and *N,N'*-diphenylcarbodiimide (R = C_6H_5, R' = C_6H_4-*p*-CH_3), with diphenyl carbonate to 210 °C yields a mixture of *s*-triazines of type **7** (see Scheme III). TLC analysis and medium-pressure liquid chromatography of the crude product showed the presence of at least three products which could not be separated cleanly. ^1H NMR spectra of the crude product show three CH_3 signals which would be in agreement with a structure **7h** but subsequent recrystallization causes changes in the CH_3 signal ratio indicating that the material is not uniform.

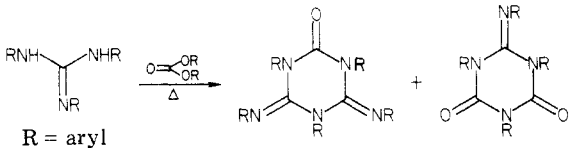
Scheme IV



Phosgene can be used in place of diphenyl carbonate to convert pentaarylbiguanides into diimino-*s*-triazinones of type **7**. Thus, treatment of a chloroform solution of **10a** (R = C_6H_5) with molar quantities of phosgene dissolved in chloroform leads to formation of a chlorocarbonyl biguanide **11**, which is cyclized to **7a** in the presence of triethylamine as a HCl scavenger (Scheme IV). This reaction is accompanied by formation of 2-(phenylimino)-1,3-diphenyl-1,3-diazetidin-4-one (**5a**) as a result of a partial dissociation of **11a** (R = C_6H_5) into *N,N'*-diphenylcarbodiimide (visible in the IR) and the *N*-(chlorocarbonyl)guanidine **12a**. (Due to this equilibrium we were not able to obtain a pure sample of **11a** for analysis.) Triethylamine treatment of crude **11a** will consequently lead to a mixture of **5a** and **7a**. Infrared spectra of the crude reaction product do show a band at 1720 cm^{-1}, a wavelength at which **5a** also absorbs. Isolation of the

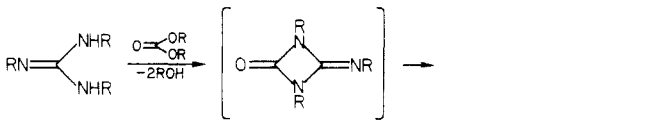
imino-1,3-diazetidinone **5a** was not attempted.

In another set of experiments we tried to use the concept of the thermally induced dissociation and recombination of guanidines to our advantage. It was hoped that the thermolysis of N^1,N^2,N^3-triarylguanidines would yield carbodiimides and arylamine which could partially recombine to give pentaarylbiguanides **10**. By carrying out these reactions in presence of diphenyl carbonate, removal of **10** by cyclocondensation was expected to yield bis(arylimino)hexahydro-*s*-triazinones of type **7**. This was indeed the case, although the reactions were not as clean as anticipated. When N^1,N^2,N^3-triphenylguanidine was heated with equimolar amounts of diphenyl carbonate to 210 °C for several minutes, phenol was given off, and 57% of **7a** could be obtained from the glassy melt on workup with methanol. On dilution of the methanolic filtrate with water, a second crop of crystals was separated which contained predominantly 2-(phenylimino)-1,3,5-triphenylhexahydro-*s*-triazine-4,6-dione (**6a**, R = C_6H_5).



7 6

Other N^1,N^2,N^3-triarylguanidines gave similar mixtures of triazines **6** and **7** which could be separated in most cases cleanly by fractional recrystallization. In addition, small amounts of *N,N'*-diarylurea could be isolated from most reaction mixtures. The appearance of compounds of type **6** among the reaction products can be explained by assuming that small amounts of aryl isocyanate are formed during the process. A possible route to RN=C=O involves the formation of the thermolabile 2-imino-1,3-diazetidinones **5** as intermediates which yield the two



5

RN=C=O + RN=C=NR

heterocumulenes RN=C=O and RN=C=NR above 120–130 °C as shown. Acylation of the remaining N^1,N^2,N^3-triarylguanidine by isocyanate and cyclization of the carbamoyl guanidine intermediate by diphenylcarbonate could well be the steps leading to compounds of type **6**. The possibility of generating **6** via a thermal equilibration of **7**, which would also involve the formation of isocyanate and carbodiimide, could be ruled out. The *s*-triazine **7a** remains unchanged on being heated for 1.5 h at 215 °C.

Experimental Section[9]

Starting Materials. The *N,N'*-diarylcarbodiimide dimers **2b** (R = C_6H_4-*p*-CH_3; mp 175–176 °C, yield 62%) and **2c** (R = C_6H_4-*p*-OCH_3; mp 178–180 °C, yield 40%)[10] were prepared in analogy to a literature procedure[2] given for the phenyl derivative **2a** (R = C_6H_5) with tri-*n*-butylphosphine as a catalyst. The pentaarylbiguanides **10b** (R = C_6H_4-*p*-CH_3; mp 115–116 °C) and **10c** (R = C_6H_4-*p*-OCH_3; mp 132 °C)[11] were prepared in high yield from the corresponding *N,N'*-diarylcarbodiimide and arylamine in a molar ratio of 2:1. N^1,N^2-Diphenyl-N^3,N^4,N^5-tri-*p*-tolylbiguanide (**10d**), prepared from *N,N'*-diphenylcarbodiimide and N^1,N^2,N^3-tri-*p*-tolylguanidine in methylene chloride, was not isolated and analyzed.

General Procedure for the Preparation of 2,4-Bis(arylimino)-1,3,5-triarylhexahydro-*s*-triazin-6-ones (7). (A) From 2,4-Bis(arylimino)-1,3-diaryl-1,3-diazetidines (2), Phosgene, and Arylamine. To an ice-cooled solution of 3.0 g (0.03 mol) of phosgene in 30 mL of methylene chloride is added with stirring at once a methylene chloride solution (10–15 mL) of 5.0 mmol of *N,N'*-diarylcarbodiimide dimer **2**. In the case of **2a**, a yellow precipitate is formed after several minutes. The reaction mixtures are kept for ~3 h at room temperature, and progress of the ring opening can be followed IR spectroscopically by disappearance of the C=N band of **2** at 1675 cm^{-1}. A new band at ~1660 cm^{-1} appears and gradually diminishes as two new ones at 1700 and 1740 cm^{-1} gain in intensity. After completed reaction, the solvent and excess phosgene are removed, and the remaining residue is redissolved in ~30 mL of methylene chloride. To this solution is added dropwise with stirring a solution of 10 mmol of arylamine in the same solvent (5–10 mL). The resulting suspensions are kept for an additional hour at room temperature, after which the solids are filtered off and the filtrates are concentrated on a rotary evaporator. The remaining oily residues are occasionally mixed with small amounts of crystals of *N,N'*-diarylurea (resulting from partial decomposition of **9**), which can be removed by dissolving the flask contents in 10–15 mL of methanol and quickly filtering off the undissolved ureas (100–200 mg). Addition of a few drops of water to the filtrate is sufficient to cause separation of crystals of **9**, which are isolated by filtration. Purity of the crude materials is checked by TLC (eluent $CHCl_3$) on silica covered plates. Samples were recrystallized for analysis from chloroform/methanol; melting points and yields are given in Table II.

(B) From N^1,N^2,N^3,N^4,N^5-Pentaarylbiguanides (10) and Diphenyl Carbonate. Mixtures of equimolar amounts of pentaarylbiguanides **10a–c** and diphenyl carbonate in the range of 5–10 mmol each are kept for 5–10 min in an oil bath which is maintained at 200–210 °C. The phenol formed during the reactions condenses on the colder parts of the flask. The glassy melts obtained are cooled and treated with 10–20 mL of methanol, leading to separation of crystals of triazines **7a,f,g** as the reaction product dissolves. The compounds thus obtained are uniform by TLC ($CHCl_3$); samples were recrystallized for analysis from chloroform/methanol; yields and melting points are given in Table II.

In one experiment, the crude pentaarylbiguanide **10d**, obtained from *N,N'*-diphenylcarbodiimide and N^1,N^2,N^3-tri-*p*-tolylguanidine (2.5 mmol each) in methylene chloride (completeness of reaction is indicated by disappearance of the IR band at 2140 cm^{-1} which is characteristic for N=C=N), is heated with equimolar amounts of diphenyl carbonate as described above. The crystalline reaction product, obtained on treatment of the melt with methanol, can be resolved partially by repeated medium-pressure liquid chromatography (ethyl acetate/hexane 2:8). Each of the fractions shows a IR spectrum characteristic of triazines of type **7**; ^1H NMR spectra ($CDCl_3$) show three CH_3 signals with differing intensity between δ 2.0 and 2.4.

(C) From N^1,N^2,N^3,N^4,N^5-Pentaphenylbiguanide (10a) and Phosgene. To an ice-cooled solution of 2.40 g (5 mmol) of **10a** and 2.0 g (0.02 mol) of triethylamine in 20 mL of chloroform is added dropwise a solution of 1.0 g (0.01 mol) of phosgene in approximately 5–10 mL of chloroform. The resulting pale yellow solution is stirred in an ice bath for 30 min followed by heating to reflux for another 1.5 h. The IR spectrum of the reaction solution shows bands at 2140 (N=C=N), 1720 (**5a**), and 1660/1640 cm^{-1} (**7a**). After removal of the solvent in vacuo a solid residue is obtained which is dissolved in 10–15 mL of methanol. Colorless crystals of **7a** soon precipitate, which are filtered off after the mixture had been allowed to stand for several hours at

(9) Melting points were taken with a Fisher-Johns melting point apparatus. Elemental analyses were by Galbraith Laboratories; spectra were recorded by using the following instruments: Beckman Acculab 4 (IR), Varian T-60 (^1H NMR), and Varian CFT-20 (^{13}C NMR).

(10) Elemental analyses gave the following values. Calcd for $C_{30}H_{28}N_4$ (**2b**): C, 81.05; H, 6.35; N, 12.60. Found: C, 81.14; H, 6.42; N, 12.38. Calcd for $C_{30}H_{28}N_4O_4$ (**2c**): C, 70.85; H, 5.55; N, 11.02. Found: C, 70.94; H, 5.61; N, 11.04.

(11) Elemental analysis gave the following values. Calcd for $C_{37}H_{37}N_5$ (**10b**): C, 80.54; H, 6.76; N, 12.70. Found: C, 80.88; H, 6.62; N, 12.50. Calcd for $C_{37}H_{37}N_5O_5$ (**10c**): C, 70.34; H, 5.90; N, 11.09. Found: C, 70.13; H, 6.01; N, 11.03.

room temperature: yield 1.40 g (55%); IR, TLC ($CHCl_3$), and mixture melting point indicate that the material is pure **7a**. No further attempts were made to isolate **5a** from the mother liquor. If the reaction is carried out in methylene chloride as solvent, cyclization of the intermediate **11a** does not take place on refluxing.

Attempts to obtain an analytically pure sample of **11a** were unsuccessful. Reprecipitation from benzene/*n*-hexane or chloroform/hexane each gave amorphous products with a softening point around 130 °C and which gave off *N,N'*-diphenylcarbodiimide (smell). Reprecipitated samples also contain small amounts of *N,N'*-diphenylcarbodiimide (IR).

(D) From N^1,N^2,N^3-Triarylguanidines and Diphenyl Carbonate. These condensations are carried out by analogy to the ones described under B. Thus, equimolar amounts of triarylguanidine and diphenyl carbonate (in the range of 5–10 mmol each) are kept for 5–10 min in a preheated oil bath at 200–210 °C. The obtained glassy melts are taken up in 10–20 mL of methanol. (Occasionally, small amounts of *N,N'*-diarylurea remain undissolved, which are removed quickly by filtration.) The solutions deposit crystals of **7** when they are allowed to stand at room temperature. The crude products, which contain only traces of imino-*s*-triazinediones **6** (TLC with $CHCl_3$ as eluent), are recrystallized for analysis from methanol; yields are given in Table II. The filtrate gives, on careful dilution with water, a second crop of crystals, which generally consist of a mixture of **6** and **7**. In the case of **6a**, a pure sample was obtained after repeated fractional recrystallization from DMF/water which was identical with a sample prepared by a described method;[6] no attempts were made to purify samples of **6f,g**.

Reactions of Aliphatic Imides with Oxalyl Chloride

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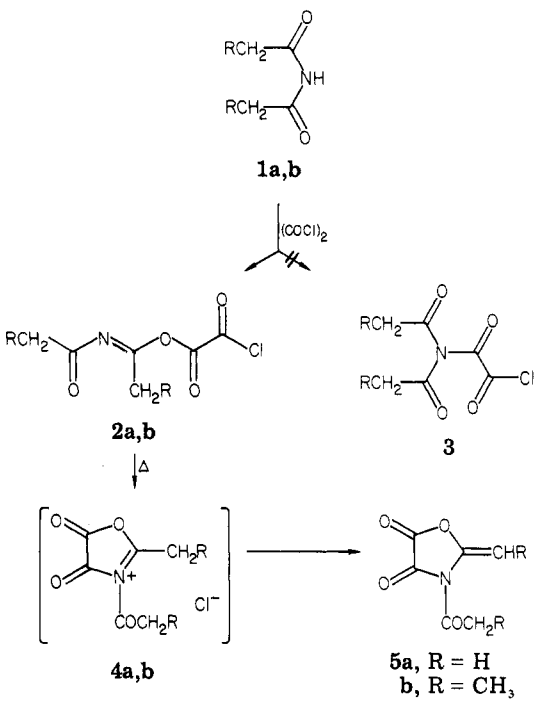
Simple aliphatic acid imides like diacetamide (**1a**), dipropionamide (**1b**), and diisobutyramide (**6**) react with oxalyl chloride with formation of O-acylated products of type **2a,b** and **7**, the structure of which was assigned on the basis of ^1H NMR and ^{13}C NMR data. Thermolysis of **2a,b** results in HCl abstraction and ring closure, giving oxazolidinediones **5a,b**. Heat treatment of **7** yields isobutyryl chloride and isobutyryl isocyanate. Glutarimide (**10a**) and adipimide (**10b**) yield fused heterocycles of type **12** directly when treated with oxalyl chloride.

Reactions of carboxylic acid amides with oxalyl chloride have been studied in detail: amides having no N-substituents were found to predominantly produce acyl isocyanates in high yields on being heated with oxalyl chloride in inert solvents.[1-5] N-Mono- and N-disubstituted amides lead to a variety of products, the nature of which depends largely upon the reaction conditions.[6,7] A thorough study about the reaction mechanism involved in the formation of O- and N-acylated products has been published by Speziale and Smith and includes a critical review of previous work on the subject.[2]

Reactions of imides with oxalyl chloride have, to our knowledge, not been studied. An investigation was undertaken to study the feasibility of preparing 2-chloro-6-oxopiperideine from glutarimide and oxalyl chloride in analogy to the related formation of imidoyl halides from amides with phosgene or thionyl chloride. The unexpected results obtained subsequently led to a study of reactions of several carboxylic acid imides with this reagent.

When diacetamide (**1a**, R = H) is heated with a slight excess of oxalyl chloride in dichloromethane solution for several hours, the starting materials are consumed, and the O-acylated product **2a** is formed in virtually quantitative yield. On following the reaction by IR, one observes that the disappearance of the carbonyl band of the imide at 1710 cm^{-1} coincides with the appearance of new bands at 1830, 1770, and 1740 cm^{-1}. The ^1H NMR spectrum of the purified product shows two signals of nearly equal intensity for the two methyl groups. This nonequivalance eliminates

Scheme I



structure **3** for the reaction product.

The O-acylated imide **2a** cyclizes on being heated in refluxing 1,2-dichloroethane to give 2-methylene-3-acetyloxazolidine-4,5-dione (**5a**). Again, the progress of the HCl abstraction can be followed by IR spectroscopy which shows the disappearance of bands characteristic of **2a** and the appearance of new bands at 1840, 1825 (double bond), 1765, 1750, and 1675 cm^{-1}. The oxazolidinedione **5a** shows two doublets for the methylene protons centered at 4.70 and 5.40 ppm each in the ^1H NMR spectrum in

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