methane in 20 mL of ether. The mixture was allowed to stand overnight at room temperature. The reaction mixture was evaporated to give an oily residue, which was subjected to column chromatography on silica gel (15 g). The column was developed with 0.3 L of chloroform–hexane (1:3) and successively with 0.3 L of chloroform–hexane (1:1).

Elution with chloroform gave 98 mg (38%) of **26**. Subsequent elution with ethyl acetate gave an oily substance, which was allowed to stand overnight at −20 °C to give a crystalline substance. Purification by recrystallization from ether–petroleum ether gave 91 mg (35%) of 4-(dimethylphosphono)-3-methoxy-4-phenyl-2-cyclopenten-1-one (**27**) as colorless needles: mp 78–80 °C; IR ($CHCl_3$) 1690 (C=O), 1605 (C=C), 1255 (P=O), 1070, 1040 (POC) $cm^{-1}$; NMR ($CDCl_3$) δ 2.58–3.70 (m, 2 H, 5-$CH_2$), 3.57 (d, 3 H, $J$ = 10.6 Hz, $POCH_3$), 3.70 (d, 3 H, $J$ = 10.6 Hz, $POCH_3$), 3.97 (s, 3 H, $OCH_3$), 5.56 (d, 1 H, $J$ = 2.0 Hz, 2-H), 7.26–7.80 (m, 5 H, aromatic protons). Anal. Calcd for $C_{14}H_{17}O_5P$: C, 56.76; H, 5.74. Found: C, 56.69; H, 5.86.

**Acknowledgment.** A part of the expenses for this work was defrayed by the Grant-in-Aid for Scientific Research of the Ministry of Education, which is gratefully acknowledged. The authors express their gratitude to Professor J. F. Bunnett of the University of California at Santa Cruz for his helpful discussions. Thanks are also due to Mrs. C. Koyanagi, Miss K. Mushiake, and Miss H. Koizumi of the Central Analyses Room of this institute for elemental analyses and spectral measurements.

**Registry No.** **4**, 28447-24-7; **5**, 26584-15-6; **6**, 16965-72-3; **7**, 41920-22-3; **8**, 39980-21-7; **9a**, 73558-63-1; **9b**, 73558-64-2; **10a**, 73558-65-3; **10b**, 73558-66-4; **11a**, 73558-67-5; **11b**, 73558-68-6; **12a**, 73558-69-7; **12b**, 73558-70-0; **13a**, 73558-71-1; **13b**, 73558-72-2; **14**, 5353-66-2; **15a**, 73558-73-3; **15b**, 73558-74-4; **16**, 73558-75-5; **17**, 73558-76-6; **18a**, 73558-77-7; **18b**, 73558-78-8; **18c**, 73558-79-9; **18d**, 73558-81-3; **19a**, 73558-81-3; **19b**, 73558-82-4; **19c**, 73558-83-5; **19d**, 73558-84-6; **20**, 73558-85-7; **21**, 73558-86-8; **22a**, 73558-87-9; **22b**, 73558-88-0; **23a**, 73558-89-1; **23b**, 73558-90-4; **24**, 73558-91-5; **25**, 73558-92-6; **26**, 73558-93-7; **27**, 73558-94-8; diketene, 674-82-8; *O*-phenylenediamine, 95-54-5; methyl acetoacetate, 105-45-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-nitroaniline, 100-01-6; *p*-chloroaniline, 106-47-8; resorcinol, 108-46-3; phloroglucinol, 108-73-6.

**Supplementary Material Available:** Listings of IR and $^1H$ NMR data for all new compounds in Tables II–IV: Table V, **9a,b–13a,b**; Table VI, **18a–d** and **19a–d**; Table VII, **22a,b** and **23a,b** (5 pages). Ordering information is given on any current masthead page.

# Reactivity of 1,3-Diimines. Reaction with Heterocumulenes

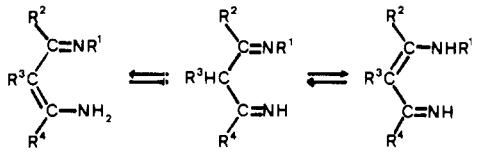
José Barluenga,* Víctor Rubio, and Vicente Gotor

*Departamento de Química Orgánica, Facultad de Ciencias, Oviedo, Spain*

*Received January 28, 1980*

1,3-Diimines **1** react with isocyanates and isothiocyanates **2** to give, as the major products, different 2-oxo- and 2-thiopyrimidines **9** and **10**. The formation of these products can be explained by two different reaction paths that involve an addition reaction followed by an electrocyclic ring closure. The nature of the group $R^1$ in **1** plays a basic role in the result of the process. Open-chain intermediate products **3** have been isolated and characterized for the first time in a cyclization reaction with diimines **1**.

Diimines **1** are readily prepared by reaction of Schiff bases with saturated nitriles in the presence of aluminum trichloride as the catalyst.[1] These diimines can be isolated in their tautomeric forms **1a** and (or) **1b**.

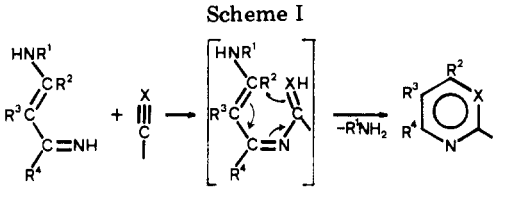


**1a** ≈ **1** ≈ **1b**

An examination of their structure shows that both tautomers can be considered to be 1-azabutadiene derivatives, and, hence, they might be suitable substrates to undergo Diels–Alder cycloadditions. This possibility is highly problematic according to results reported in the references, since 1-azabutadiene derivatives show, in general, little aptitude to give this type of cycloaddition.[2]

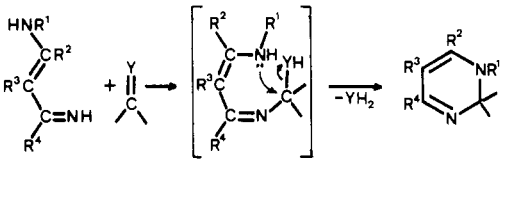
Our own experiments on the reactivity of **1** fully support those results previously reported for 1-azabutadiene derivatives; the reaction of **1** with excellent dienophiles, such as tetracyanoethylene[3] or azodicarboxylic acid ester,[4] affords products whose structure does not correlate with that of cycloaddition adducts.

Scheme I



X = N, C-$CO_2$Et

Scheme II



Y = NR, O, $(OEt)_2$

However, diimines **1** react with saturated nitriles and acetylenedicarboxylic acid ester to give rise to convenient synthetic methods for the preparation of pyrimidines[5] and pyridines,[6] respectively. Although these compounds could

(1) H. Hoberg and J. Barluenga, *Synthesis*, 142 (1970).
(2) C. M. Gladstone, P. H. Daniels, and J. L. Wong, *J. Org. Chem.*, **42**, 1375 (1977).
(3) V. Rubio, Ph. D. Thesis, Universidad de Oviedo, 1979.
(4) J. Barluenga, Universidad de Oviedo, 1978.
(5) H. Hoberg and J. Barluenga, *Synthesis*, 363 (1970).

0022-3263/80/1945-2592$01.00/0 

Table I. Reactions of Diimines 1 with Heterocumulenes 2

| 1[a] | | 2 | | molar ratio | time, | temp, | yield, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^4$ | $R^5$ | Z | of 1/2 | h | °C | 3 | 4 | 9 | 10 | 11 | products |
| $C_6H_5$ | $C_6H_5$ | c-$C_6H_{11}$ | O | 1:1.5 | 24 | 80 | 50 | | | 45 | | 3a, 10a |
| *p*-$CH_3C_6H_4$ | $C_6H_5$ | c-$C_6H_{11}$ | O | 1:1.5 | 24 | 25 | 25 | | | 20 | | 3b, 10b |
| c-$C_6H_{11}$ | *p*-$CH_3C_6H_4$ | $C_6H_5$ | O | 1:1.5 | 3 | 80 | | 10 | 75 | | | 4a, 9a |
| *p*-$CH_3C_6H_4$ | $C_6H_5$ | $C_6H_5$ | O | 1:1.5 | 8 | 80 | | | 44 | 36 | | 9b (≡10a), 10b |
| *o*-$CH_3C_6H_4$ | $C_6H_5$ | $C_6H_5$ | O | 1:1.5 | 8 | 80 | | | 40 | 40 | | 9b (≡10a), 10c |
| c-$C_6H_{11}$ | *p*-$CH_3C_6H_4$ | c-$C_6H_{11}$ | O | 1:2 | 8 | 80 | 60 | 17 | | | | 3c, 4b |
| c-$C_6H_{11}$ | $C_6H_5$ | c-$C_6H_{11}$ | O | 1:1 | 8 | 80 | 80 | | | | | 3d |
| c-$C_6H_{11}$ | $C_6H_5$ | *n*-$C_4H_9$ | O | 1:1 | 48[b] | 80 | | | 80 | | | 9c |
| c-$C_6H_{11}$ | *p*-$CH_3C_6H_4$ | $C_6H_5$ | S | 1:1 | 24 | 25 | | | 95 | | | 9d |
| c-$C_6H_{11}$ | $C_6H_5$ | c-$C_6H_{11}$ | S | 1:1 | 24 | 80 | | | 65 | | | 9e |
| *o*-$CH_3C_6H_4$ | *p*-$CH_3C_6H_4$ | $C_6H_5$ | S | 1:1 | 24 | 80 | | | 75 | | 10 | 9d, 11a |
| *p*-$CH_3C_6H_4$ | $C_6H_5$ | $C_6H_5$ | S | 1:1 | 24 | 80 | | | 80 | | 8 | 9f, 11b |
| $C_6H_5$ | $C_6H_5$ | c-$C_6H_{11}$ | S | 1:1 | 72 | 80 | | | | | | |

[a] $R^2 = C_6H_5$; $R^3$ = Me. [b] In the presence of $AlCl_3$.

be generated by a Diels–Alder cycloaddition, from the results mentioned above and the fact that nitriles are poor dienophiles in such processes[7] it is more likely to suppose an addition reaction followed by an electrocyclic ring closure as the operative pathway to afford the heterocyclization products (Scheme I).

Substituted dihydropyrimidines are obtained by reaction of diimines 1 with Schiff bases,[8] aldehydes, acetals, and ketals.[9] The formation of these heterocycles proceeds through a condensation reaction (Scheme II).

The easy access to diimines 1 and their striking reactivity makes them convenient starting materials for the synthesis of various six-membered-ring heterocycles containing one or more heteroatoms.

In the present paper, the reaction of 1 with heterocumulenes is studied. Intermediate products were isolated for the first time in a heterocyclization of 1 and the mechanism of the process is discussed on the basis of these compounds.

## Results and Discussion

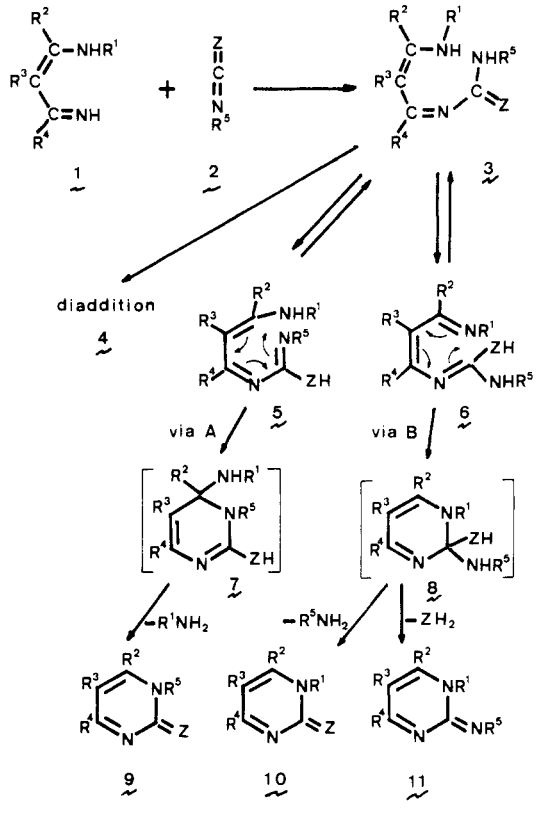
**Reaction with Isocyanates.** Diimines 1 react with isocyanates 2 (Z = O) at room temperature to yield different 2-oxopyrimidines 9 and (or) 10 as the major products. *N,N'*-Disubstituted ureas resulting from the addition of amine to isocyanate and, in some instances, the monoaddition compound 3 as well as other products of higher molecular weight, 4, are also obtained (see Table I). NMR and mass spectroscopic data of compounds 4 correlated with those expected for the adduct resulting from interaction between 1 mol of diimine 1 and 2 mol of isocyanate 2.[10] The structures of 9 and 10 were corroborated by an alternative synthesis.[11]

The formation of 9 and 10 can be easily explained by two alternative reaction paths, A and B (see Scheme III). The course of the process through A or B depends on the structure of $R^1$ and $R^5$.

Mixtures of pyrimidones 9 and 10 are produced, to a similar extent, when both $R^1$ and $R^5$ are aromatic groups.

When $R^1$ and $R^5$ are aromatic and aliphatic groups, respectively, pyrimidones 10 are obtained as the sole

Scheme III




heterocyclic products. Besides these, open-chain compounds 3 which were characterized by NMR, IR, and mass spectrometry were also isolated. This structure could not be corroborated by chemical methods since treatment of 3 with 6 N $H_2SO_4$ gave the pyrimidone 10; the same compound results by heating of 3.

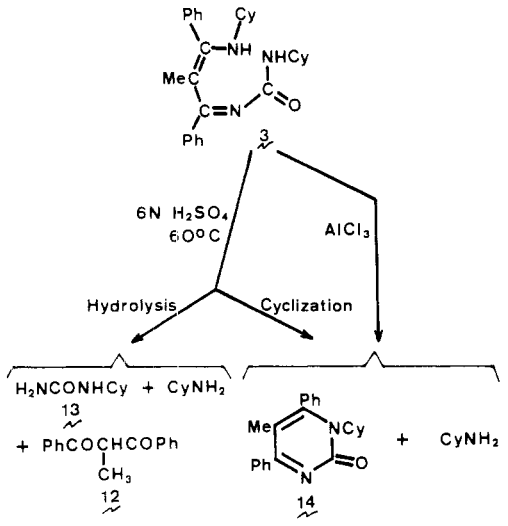
When $R^1$ and $R^5$ are aliphatic and aromatic groups, respectively, pyrimidones 9 are obtained. The presence of 10 could not be detected. Small amounts of diaddition products 4 were also generated.

In contrast, mixtures of open-chain products 3 and 4, in which 3 predominates, are obtained when both $R^1$ and $R^5$ are aliphatic groups.

Treatment of 3 ($R^1 = R^5$ = c-$C_6H_{11}$) with 6 N aqueous sulfuric acid yielded a mixture of products as a result of two competitive processes: acid-promoted cyclization and hydrolysis (see Scheme IV). The hydrolysis products were identified as the diketone 12, cyclohexylurea 13, and cyclohexylamine which corroborate, along with its spectral IR, NMR and mass spectral data, the structure previously

(6) J. Barluenga, S. Fustero, and V. Gotor, *Synthesis*, 191 (1975).
(7) S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, 62, 405 (1962).
(8) V. Gomez Aranda, J. Barluenga, V. Gotor, and S. Fustero, *Synthesis*, 720 (1974).
(9) J. Barluenga, M. Tomas, S. Fustero, and V. Gotor, *Synthesis*, 346 (1979).
(10) Attempts to elucidate the structure of 4 by acid hydrolysis led to a definite new compound whose nature could not be clearly established by NMR, IR, and mass spectroscopic analyses.
(11) J. Barluenga, V. Rubio, M. Tomas, and V. Gotor, *J. Chem. Soc., Chem. Commun.*, 675 (1979).

Scheme IV




assumed for **3**. Cyclization products also are obtained in good yields by treatment of **3** with aluminum trichloride.

The structure of the isolated product **3** supports the hypothesis that 1,3-diimines **1** first react, in a general way, on the less substituted nitrogen atom.

The above results can be easily rationalized if we assume that **3** will also exist in two tautomeric forms, **5** and **6**. The tautomer **5** will predominate when $R^1$ is aliphatic and $R^5$ is aromatic since it allows a more extended conjugation; the electrocyclic ring closure of **5** followed by a loss of amine leads to **9**. For the same reason **6** will predominate when $R^1$ is aromatic and $R^5$ is aliphatic, and, hence, **10** is obtained in this case. Compounds **11** could never be detected.

When $R^1$ and $R^5$ are aromatic groups, **5** and **6** are compounds of similar stability, and, consequently, the process takes place via A and B simultaneously to give a mixture of pyrimidones **9** and **10**.

On the other hand, when $R^1$ and $R^5$ are aliphatic groups the monoaddition product will predominantly exist as the tautomer **3**, and it will only undergo the cyclization process in the presence of an acid catalyst. The reaction between **1** ($R^1$ = c-$C_6H_{11}$) and **2** ($R^5$ = *n*-butyl) in the presence of $AlCl_3$ led exclusively to the pyrimidone **9c**; this fact clearly shows that in this case only the reaction path A is operative.

**Reaction with Isothiocyanates.** The reaction of 1,3-diimines **1** ($R^1$ = aliphatic) with isothiocyanates **2** (Z = S, $R^5$ = aliphatic or aromatic) leads exclusively to 2-thiopyrimidines **9**, and, hence, it takes place through path A; when $R^5$ is an aromatic group, the reaction resembles that with isocyanates (Z = O), and the sole formation of **9** can also be explained in this case in a similar way. However, when $R^5$ is an aliphatic group, cyclic compounds **9** are directly obtained even in the absence of a catalyst. With isocyanates, open-chain compounds **3** and **4** were obtained under similar reaction conditions. The greater double bond character of the C–N linkage in thioamides than that in amides[12] accounts for the predominancy of the tautomer **5** in the equilibria when Z = S, and, consequently, the cyclization process is more favorable than in the case of isocyanates (Z = O).

When both $R^1$ and $R^5$ are aromatic groups, besides thiopyrimidines **9**, dihydropyrimidines **11** are obtained as minor products. Since $R^1$ is aryl, tautomer **6** will be better stabilized than in previously studied cases, and for this reason the reaction can also proceed via B. The cyclic intermediate **8** (not isolated) in this case yields **11** by elimination of $H_2S$.

When $R^1$ and $R^5$ are aryl and alkyl, respectively, the reaction does not take place. This finding can be rationalized by the following reasons: (a) aliphatic isothiocyanates are less reactive than their aromatic homologues; (b) the basicity of the imine nitrogen in 1,3-diimines **1** is decreased by the presence of aromatic groups attached to the amine nitrogen.

## Conclusions

Diimines **1** react by their imine nitrogen with isocyanates and isothiocyanates to afford, in a first step, an open-chain addition compound whose structure has been clearly established in some instances; this intermediate undergoes two types of 6 $\pi$ electrocyclic ring closure to yield different heterocyclic products. The nature of the group $R^1$ attached on the amine nitrogen in **1** plays a predominant role in the result of the process.

The proposed mechanism, addition followed by electrocyclic ring closure, can also explain the formation of the pyridines[6] and pyrimidines[5] previously described and corroborates the little aptitude of 1-azabutadiene derivatives to undergo (4 + 2) cycloadditions.

## Experimental Section

**General Methods.** Melting points are uncorrected. The NMR spectra were determined in deuterated chloroform by using a Varian EM-390 spectrometer (90 MHz) with internal tetramethylsilane as the reference. Infrared spectra were recorded in a Nujol suspension on a Pye Unicam SP-1000 spectrophotometer. Mass spectra were taken on a Hewlett-Packard 5930 A spectrometer. Microanalyses were performed on a Perkin-Elmer Model 240. GC analyses were performed on a Varian Aerograph 2800 instrument equiped with an OV-101 Chromosorb column.

Physical and spectral data of the compounds prepared are given in Table II.

**Materials.** 1,3-Diimines were prepared according to literature methods.[1] All the other reagents were commercially available (99+%) and were used as received. Tetrahydrofuran was distilled from sodium–benzophenone under argon prior to use.

**1,2-Dihydro-5-methyl-2-oxo-1,4,6-triphenylpyrimidine (10a) and *N*-Cyclohexyl-*N'*-(2-methyl-1,3-diphenyl-3-(phenylamino)-2-propenylidene)urea (3a).** A mixture of 3-imino-2-methyl-*N*,1,3-triphenylprop-1-en-1-amine (3.12 g, 10 mmol) and cyclohexyl isocyanate (1.85 g, 15 mmol) in anhydrous tetrahydrofuran (50 mL) was refluxed for 24 h and then slowly added to 200 mL of ice-cooled 2 N $H_2SO_4$. The resulting mixture was extracted with ether, and the organic layer was dried over sodium sulfate, filtered, and evaporated. The residue was separated by silica gel column chromatography using chloroform–acetone (91:9) as eluent. Three fractions were isolated. The first fraction gave 2.18 g (50% based on **1**) of **3a**.

Anal. Calcd for $C_{29}H_{31}N_3O$: C, 79.60; H, 7.14; N, 9.60. Found C, 79.73; H, 6.95; N, 9.47.

From the second fraction 0.2 g of *N,N'*-dicyclohexylurea was obtained; mp 228–230 °C (lit. mp 229 °C).

The eluent was removed from the third fraction, and the solid residue was crystallized from hexane–chloroform to give 1.52 g (45% based on **1**) of **10a**.

Anal. Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.65; H, 5.42; N, 8.14.

**1,2-Dihydro-5-methyl-2-oxo-4,6-diphenyl-1-(*p*-tolyl)pyrimidine (10b) and *N*-Cyclohexyl-*N'*-[2-methyl-1,3-diphenyl-3-(*p*-tolylamino)-2-propenylidene]urea (3b).** A solution of 3-imino-2-methyl-1,3-diphenyl-*N*-(*p*-tolyl)prop-1-en-1-amine (2.26 g, 10 mmol) and cyclohexyl isocyanate (1.85 g, 15 mmol) in anhydrous tetrahydrofuran (50 mL) was stirred at room temperature for 24 h. Two fractions were obtained by using the above procedure.

(12) W. Walter and J. Voss, "The Chemistry of Amides", S. Patai, Ed., Interscience, London, 1970, p 414, and references cited therein.

Table II. Physical and Spectral Data

| compd | mp, °C | IR (Nujol) $\nu$, $cm^{-1}$ | NMR ($CDCl_3$), $\delta$ | MS ($M^+$), m/e |
|---|---|---|---|---|
| 3a | 82-84 | 1660, 3310, 3390 | 0.8-2.0 (m, 10 H), 1.75 (s, $CH_3$), 1.95 (s, $CH_3$), 3.0-4.0 (m, CH), 5.9 (s, NH), 6.1 (s, NH), 7.0-8.1 (m, 15 H, Ar H) | 437 |
| 3b | 186-188 | 1650, 3390, 3400 | 0.9-2.0 (m, 10 H), 1.75 (s, $CH_3$), 1.95 (s, $CH_3$), 2.3 (s, $CH_3$), 2.35 (s, $CH_3$), 3.2-4.2 (m, CH), 6.4 (s, NH), 6.6 (s, NH), 6.9-8.0 (m, 14 H, Ar H) | |
| 3c | 125-127 | 1660, 3300, 3380 | 0.8-2.0 (m, 23 H), 2.3 (s, $CH_3$), 2.4 (s, $CH_3$), 3.2-3.8 (m, CH), 4.2-4.7 (m, CH), 5.9 (s, NH), 6.5 (s, NH), 7.0-8.0 (m, 9 H, Ar H) | |
| 3d | 156-158 | 1650, 3300, 3400 | 0.9-2.0 (m, 20 H), 1.9 (s, $CH_3$), 2.0 (s, $CH_3$), 3.0-4.0 (m, 2 CH), 5.8 (s, NH), 6.1 (s, NH), 7.1-7.9 (m, 10 H, Ar H) | 443 |
| 4a | 173-175 | 1670, 1685, 3350, 3400 | 0.9-2.0 (m, 10 H), 2.1 (s, $CH_3$), 2.5 (s, $CH_3$), 4.2-4.5 (m, CH), 6.5 (s, NH), 7.0-8.0 (m, 19 H, Ar H), 8.5 (s, NH) | 570 |
| 4b | 169-171 | 1650, 3250, 3350 | 0.9-2.1 (m, 30 H), 1.9 (s, $CH_3$), 2.4 (s, $CH_3$), 3.1-3.4 (m, CH), 3.7-4.0 (m, CH), 4.1-4.4 (m, CH), 6.4 (s, NH), 6.7 (s, NH), 7.0-8.0 (m, 9 H, Ar H) | |
| 9a | 180-182 | 1680 | 1.9 (s, $CH_3$), 2.4 (s, $CH_3$), 7.0-7.8 (m, 14 H, Ar H) | |
| 9c | 108-110 | 1675 | 0.8 (t, $CH_3$), 1.0-1.4 (m, $CH_2$), 1.6-1.9 (m, $CH_2$), 1.8 (s, $CH_3$), 3.8 (t, $CH_2$), 7.3-7.8 (m, 10 H, Ar H) | |
| 9d | 258-260 | 1580, 1590 | 1.83 (s, $CH_3$), 2.31 (s, $CH_3$), 6.9-7.9 (m, 14 H, Ar H) | |
| 9e | 221-223[a] | 1570, 1575 | 0.8-1.9 (m, 8 H), 1.7 (s, $CH_3$), 2.2-2.7 (m, 2 CH), 4.6-5.0 (m, CH), 7.0-7.7 (m, 10 H, Ar H) | |
| 9f | 296-298[b] | 1580, 1585 | 1.91 (s, $CH_3$), 7.0-7.8 (m, 15 H, Ar H) | |
| 10a | 212-214[c] | 1680 | 1.85 (s, $CH_3$), 7.0-7.8 (m, 15 H, Ar H) | |
| 10b | 219-221 | 1685 | 1.88 (s, $CH_3$), 2.25 (s, $CH_3$), 6.9-7.8 (m, 14 H, Ar H) | |
| 11a | 175-177 | 1600, 1620 | 1.8 (s, $CH_3$), 2.3 (s, $CH_3$), 2.32 (s, $CH_3$), 6.9-7.7 (m, 18 H, Ar H) | 441 |
| 11b | 196-198 | 1580, 1620 | 1.8 (s, $CH_3$), 2.3 (s, $CH_3$), 7.0-7.8 (m, 19 H, Ar H) | |
| 14 | 194-196[d] | 1670 | 0.9-1.9 (m, 8 H), 1.75 (s, $CH_3$), 2.5-3.0 (m, 2 CH), 3.3-3.8 (m, CH), 7.2-7.7 (m, 10 H, Ar H) | |

[a] Lit.[11] mp 221-223 °C. [b] Lit.[11] mp 298-299 °C. [c] Lit.[11] mp 213-215 °C. [d] Lit.[11] mp 194-196 °C.

The first fraction afforded 1.12 g (25% based on **1**) of **3b**.

Anal. Calcd for $C_{30}H_{33}N_3O$: C, 79.79; H, 7.37; N, 9.30. Found: C, 80.01; H, 7.16; N, 9.15.

The second fraction was recrystallized from hexane–chloroform to give 0.7 g (20% based on **1**) of **10b**.

Anal. Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 82.03; H, 5.45; N, 7.86.

**Treatment of 3a with 6 N Sulfuric Acid.** A solution of *N*-cyclohexyl-*N'*-[2-methyl-1,3-diphenyl-3-(phenylamino)-2-propenylidene]urea (**3a**; 2.18 g, 5 mmol) in 6 N $H_2SO_4$ (70 mL) was heated at 60 °C for 6 h. The solution was treated with ice-cooled concentrated KOH solution until basic, extracted with ether, and evaporated to give 1.18 g (70%) of **10a**, mp 213–215 °C.

**Conversion of 3a to 10a.** A solution of **3a** (2.18 g, 5 mmol) in anhydrous tetrahydrofuran (50 mL) was refluxed for 4 days. The solution was evaporated to dryness in vacuo, and the solid obtained was recrystallized from hexane–chloroform to afford 1 g (65%) of **10a**, mp 212–214 °C.

**1,2-Dihydro-5-methyl-2-oxo-1,6-diphenyl-4-(*p*-tolyl)pyrimidine (9a).** A mixture of *N*-cyclohexyl-3-imino-2-methyl-1-phenyl-3-(*p*-tolyl)prop-1-en-1-amine (3.32 g, 10 mmol) and phenyl isocyanate (1.7 g, 15 mmol) in anhydrous tetrahydrofuran (70 mL) was heated at 80 °C for 3 h. The solution was poured into 200 mL of ice-cooled 2 N $H_2SO_4$, extracted with ether, dried over sodium sulfate, and concentrated. The residue was separated by silica gel column chromatography using chloroform–acetone (91:9) as eluent. Three fractions were isolated. From the first fraction 0.5 g (10% based on **1**) of **4a** was obtained.

Anal. Calcd for $C_{37}H_{38}N_4O_2$: C, 77.86; H, 6.71; N, 9.81. Found: C, 78.13; H, 6.50; N, 9.56.

The second fraction gave 0.2 g of *N*-cyclohexyl-*N'*-phenylurea.

The eluent was removed from the third fraction, and the solid residue was crystallized from hexane–chloroform to give 2.64 g (75%) of **9a**.

Anal. Calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 81.92; H, 5.67; N, 8.05.

**1,2-Dihydro-5-methyl-2-oxo-1,4,6-triphenylpyrimidine (9b ≡ 10a) and 1,2-Dihydro-5-methyl-2-oxo-4,6-diphenyl-1-(*p*-tolyl)pyrimidine (10b).** A solution of 3-imino-2-methyl-1,3-diphenyl-*N*-(*p*-tolyl)prop-1-en-1-amine (3.26 g, 10 mmol) and phenyl isocyanate (1.7 g, 15 mmol) in anhydrous tetrahydrofuran (70 mL) was refluxed for 8 h and then slowly added to 200 mL of ice-cooled 2 N $H_2SO_4$, the mixture was extracted with ether, and the organic layer dried over sodium sulfate. The solution was concentrated and the residue fractionally recrystallized from hexane. The first fractions were washed with benzene and filtered out. The filtrate was evaporated and recrystallized from hexane to give 1.55 g (44%) of **9b** (≡**10a**), mixture melting point with **10a** 211–213 °C. The later fractions were identified as **10b** (1.21 g, 36%).

**1,2-Dihydro-5-methyl-2-oxo-1,4,6-triphenylpyrimidine (9b ≡ 10a) and 1,2-Dihydro-5-methyl-2-oxo-4,6-diphenyl-1-(*o*-tolyl)pyrimidine (10c).** A solution of 3-imino-2-methyl-1,3-diphenyl-*N*-(*o*-tolyl)prop-1-en-1-amine (3.26 g, 10 mmol) and phenyl isocyanate (1.7 g, 15 mmol) in anhydrous tetrahydrofuran (70 mL) was heated at 80 °C for 8 h. The mixture was added to 200 mL of ice-cooled 2 N $H_2SO_4$, extracted with ether, dried, and evaporated. The residue was recrystallized from hexane–chloroform to give a mixture of **9b** (≡**10a**; 40%) and **10c** (40%) according to their NMR and mass spectral data.

***N*-Cyclohexyl-*N'*-[3-(cyclohexylamino)-2-methyl-3-phenyl-1-(*p*-tolyl)-2-propenylidene]urea (3c).** A solution of *N*-cyclohexyl-3-imino-2-methyl-1-phenyl-3-(*p*-tolyl)prop-1-en-1-amine (3.32 g, 10 mmol) and cyclohexyl isocyanate (2.5 g, 20 mmol) in anhydrous tetrahydrofuran was refluxed for 8 h. The mixture was poured into 150 mL of 2 N $H_2SO_4$ and extracted with ether. The organic layer was concentrated to give a solid which was purified by silica gel column chromatography (chloroform–acetone 91:9 as eluent) to afford 0.98 g (17% based on **1**) of **4b**.

Anal. Calcd for $C_{37}H_{50}N_4O_2$: C, 76.25; H, 8.65; N, 9.61. Found: C, 76.49; H, 8.40; N, 9.47.

The aqueous layer was treated with 3 N KOH until basic and then extracted with ether. The ethereal solution was concentrated and recrystallized from hexane–THF to give 2.73 g (60%) of **3c**.

Anal. Calcd for $C_{30}H_{39}N_3O$: C, 78.73; H, 8.59; N, 9.18. Found: C, 79.03; H, 8.36; N, 8.39.

***N*-Cyclohexyl-*N'*-[3-(cyclohexylamino)-2-methyl-1,3-diphenyl-2-propenylidene]urea (3d).** A mixture of *N*-cyclohexyl-3-imino-2-methyl-1,3-diphenylprop-1-en-1-amine (3.18 g, 10 mmol) and cyclohexyl isocyanate (1.25 g, 10 mmol) in anhydrous tetrahydrofuran (70 mL) was heated at 80 °C for 8 h. The solution was concentrated and the residue recrystallized from hexane–chloroform to give 3.5 g (80%) of **3d**.

Anal. Calcd for $C_{29}H_{37}N_3O$: C, 78.51; H, 7.73; N, 9.47. Found: C, 78.86; H, 7.38; N, 9.30.

**Treatment of 3d with 6 N Sulfuric Acid.** A solution of **3d** (4.43 g, 10 mmol) in 6 N $H_2SO_4$ (70 mL) was heated at 60 °C for 6 h and then extracted with ether, and the organic layer was concentrated. Recrystallization from hexane of the solid residue afforded 2-methyl-1,3-diphenylpropan-1,3-dione (**12**): 1.4 g (60%); mp 83–85 °C (lit. mp 85 °C). The acid layer was treated with concentrated KOH solution until basic, extracted with ether, and evaporated to give 0.9 g of cyclohexylamine (GC) and a residue which was washed with hot water to remove **13** and recrystallized from hexane–chloroform to yield 1-cyclohexyl-1,2-dihydro-5-methyl-2-oxo-4,6-diphenylpyrimidine (**14**; 1.34 g, 40%).

Anal. Calcd for $C_{23}H_{24}N_2O$: C, 80.20; H, 7.02; N, 8.13. Found: C, 80.39; H, 6.87; N, 7.89.

*N*-Cyclohexylurea (**13**; 0.8 g, 60%) was precipitated from the aqueous solution by partial evaporation; mp 194–196 °C.

**Treatment of 3d with Aluminum Trichloride.** Aluminum trichloride (0.66 g, 5 mmol) was added under an argon atmosphere to a well-stirred solution of **3d** (2.2 g, 5 mmol) in anhydrous tetrahydrofuran (50 mL). The mixture was heated at 80 °C for 48 h and then slowly added to 200 mL of ice-cooled 3 N KOH. The resulting mixture was extracted with ether, and the organic layer was dried over sodium sulfate, filtered, and evaporated. The residue was crystallized from hexane–chloroform to give 1.37 g (80%) of **14**.

**1-(*n*-Butyl)-1,2-dihydro-5-methyl-2-oxo-4,6-diphenylpyrimidine (9c).** Aluminum trichloride (1.33 g, 10 mmol) was slowly added under an argon atmosphere to a solution of *N*-cyclohexyl-3-imino-2-methyl-1,3-diphenylprop-1-en-1-amine (3.18 g, 10 mmol) and *n*-butyl isocyanate (1 g, 10 mmol) in anhydrous tetrahydrofuran. The mixture was heated at 80 °C for 48 h, treated with 180 mL of 3 N KOH, and extracted with ether. The organic layer was evaporated and crystallized from hexane–THF to afford 2.5 g (80%) of **9c**.

Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.37; H, 7.13; N, 9.05.

**1,2-Dihydro-5-methyl-1,6-diphenyl-4-(*p*-tolyl)-2-thiopyrimidine (9d).** A mixture of *N*-cyclohexyl-3-imino-2-methyl-1-phenyl-3-(*p*-tolyl)prop-1-en-1-amine (3.32 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) was stirred at room temperature for 24 h. The solution was then acidified with 2 N $H_2SO_4$ (200 mL) and extracted with ether. The dry organic layer was evaporated and the residue recrystallized from hexane–THF to afford 3.5 g (95%) of **9d**.

Anal. Calcd for $C_{24}H_{20}N_2S$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.05; H, 5.45; N, 7.45.

**1-Cyclohexyl-1,2-dihydro-5-methyl-4,6-diphenyl-2-thiopyrimidine (9e).** A solution of *N*-cyclohexyl-3-imino-2-methyl-1,3-diphenylprop-1-en-1-amine (3.18 g, 10 mmol) and cyclohexyl isothiocyanate (1.41 g, 10 mmol) in anhydrous tetrahydrofuran was refluxed for 24 h. The mixture was then cooled, acidified with 2 N sulfuric acid (200 mL), and extracted with ether. The dry organic layer was evaporated and the residue recrystallized from hexane–THF to give 2.34 g (65%) of **9e**.

Anal. Calcd for $C_{23}H_{24}N_2S$: C, 76.63; H, 6.71; N, 7.77. Found: C, 76.59; H, 6.75; N, 7.79.

**1,2-Dihydro-5-methyl-1,6-diphenyl-4-(*p*-tolyl)-2-thiopyrimidine (9d) and 1,2-Dihydro-5-methyl-2-(phenylimino)-1-(*o*-tolyl)-4-(*p*-tolyl)pyrimidine (11a).** A solution of 3-imino-2-methyl-1-phenyl-*N*-(*o*-tolyl)-3-(*p*-tolyl)prop-1-en-1-amine (3.40 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in anhydrous tetrahydrofuran was heated at 80 °C for 24 h. The mixture was then added to 200 mL of 2 N sulfuric acid and the mixture extracted with ether. The ethereal solution was concentrated and the residue crystallized from hexane–THF to give 2.76 g (75%) of **9d**. The acid solution was treated with 3 N KOH until basic and extracted with ether. The organic layer was concentrated and the residue crystallized from hexane–THF to give 0.73 g (10%) of **11a**.

Anal. Calcd for $C_{31}H_{27}N_3$: C, 84.32; H, 6.16; N, 9.52. Found: C, 84.56; H, 5.98; N, 9.46.

**1,2-Dihydro-5-methyl-1,4,6-triphenyl-2-thiopyrimidine (9f) and 1,2-Dihydro-5-methyl-1,4-diphenyl-2-(phenylimino)pyrimidine (11b).** A solution of 3-imino-2-methyl-1,3-diphenyl-*N*-(*p*-tolyl)prop-1-en-1-amine (3.26 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) in anhydrous tetrahydrofuran was heated at 80 °C for 24 h and treated as above. From the organic layer 2.8 g (80%) of **9f** was obtained.

Anal. Calcd for $C_{23}H_{18}N_2S$: C, 77.93; H, 5.12; N, 7.90. Found: C, 78.12; H, 4.96; N, 7.77.

From the acid solution 0.3 g (8%) of **11b** was obtained.

Anal. Calcd for $C_{30}H_{25}N_3$: C, 84.28; H, 5.89; N, 9.83. Found: C, 84.46; H, 5.62; N, 9.71.

**Reaction of *N*-Aryl-Substituted 1,3-Diimines with Cyclohexyl Isothiocyanate.** A solution of 3-imino-2-methyl-*N*,1,3-triphenylprop-1-en-1-amine (3.12 g, 10 mmol) and cyclohexyl isothiocyanate (1.41 g, 10 mmol) in anhydrous tetrahydrofuran (70 mL) was boiled for 3 days. After evaporation of the solution the starting materials were recovered.

**Registry No.** **1** ($R^1 = R^2 = R^4 = C_6H_5$, $R^3$ = Me), 71115-28-1; **1** ($R^1 = p$-$CH_3C_6H_4$, $R^2 = R^4 = C_6H_5$, $R^3$ = Me), 71115-30-5; **1** ($R^1 = c$-$C_6H_{11}$, $R^2 = C_6H_5$, $R^3$ = Me, $R^4 = p$-$CH_3C_6H_4$), 71115-26-9; **1** ($R^1 = o$-$CH_3C_6H_4$, $R^2 = R^4 = C_6H_5$, $R^3$ = Me), 71115-33-8; **1** ($R^1 = c$-$C_6H_{11}$, $R^2 = R^4 = C_6H_5$, $R^3$ = Me), 71115-27-0; **1** ($R^1 = o$-$CH_3C_6H_4$, $R^2 = C_6H_5$, $R^3$ = Me, $R^4 = p$-$CH_3C_6H_4$), 71115-25-8; **2** ($R^5 = c$-$C_6H_{11}$, Z = O), 3173-53-3; **2** ($R^5 = C_6H_5$, Z = O), 103-71-9; **2** ($R^5 = n$-$C_4H_9$, Z = O), 111-36-4; **2** ($R^5 = C_6H_5$, Z = S), 103-72-0; **2** ($R^5 = c$-$C_6H_{11}$, Z = S), 1122-82-3; **3a**, 73557-73-0; **3b**, 73557-74-1; **3c**, 73557-75-2; **3d**, 73557-76-3; **4a**, 73557-77-4; **4b**, 73557-78-5; **9a**, 73557-79-6; **9b**, 72923-14-9; **9c**, 73557-80-9; **9d**, 73557-81-0; **9e**, 72923-21-8; **9f**, 73557-81-0; **10b**, 73557-82-1; **10c**, 73557-83-2; **11a**, 73557-84-3; **11b**, 73557-85-4; **12**, 1846-29-3; **13**, 698-90-8; **14**, 72923-13-8; *N,N'*-dicyclohexylurea, 2387-23-7; *N*-cyclohexyl-*N'*-phenylurea, 886-59-9.