Methyl-*tert*-butylcarbodiimide. A Diagnostic Tool in 2 + 2 Cycloaddition Reactions[1]

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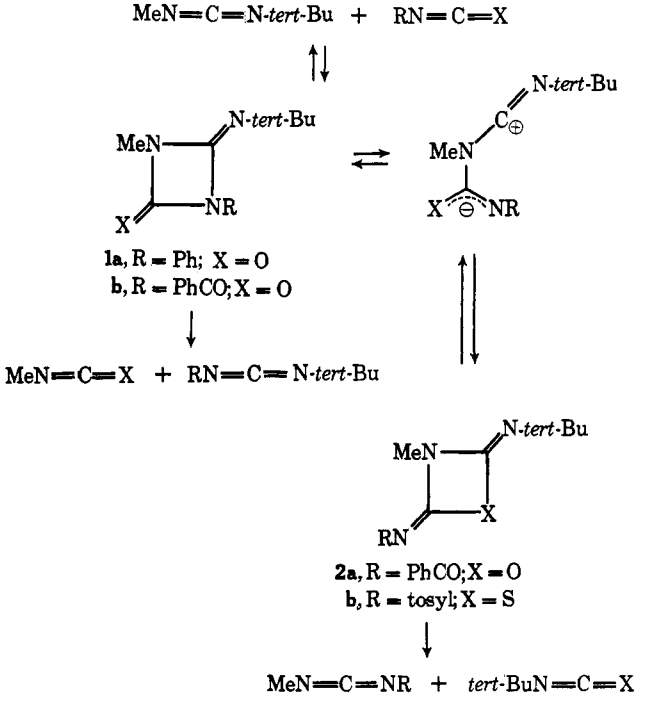
Abstract: Fragmentation of 2 + 2 cycloadducts derived from methyl-*tert*-butylcarbodiimide and other heterocumulenes allows assignment of structure for the heterocyclic four-membered ring adducts. While aryl isocyanates and arenesulfonyl isocyanates add across their C=N double bond, benzoyl isocyanate adds across the cumulative C=O double bond. Reactive isothiocyanates, such as 4-nitrophenyl, tosyl, and ethyl isothiocyanatoformate, add across their C=S double bond, and *N*-sulfinylsulfonamides add across their N=S double bond. The retro 2 + 2 process was used to reassign the structures of the 2 + 2 cycloadducts derived from carbodiimides and benzoyl isocyanate and isothiocyanates, respectively.

In the reaction of stoichiometric amounts of a carbodiimide and another heterocumulene two isomeric 2 + 2 cycloadducts are possible. Only in cases where the developing charges in the initial bond formation step are sufficiently delocalized, linear 1:1 adducts are formed which can undergo a 1,4-dipolar cycloaddition reaction to produce six-membered ring heterocycles. For example, in the reaction of arenesulfonyl isocyanates with carbodiimides only six-membered ring 2 + 2 + 2 cycloadducts were isolated.[2]

Presently, proof of structure of the heterocyclic 2 + 2 cycloadducts rests solely on spectral data and only rarely have ring opening experiments been conducted. It is the purpose of our investigation to provide a simple fragmentation method which would allow differentiation between the isomeric four-membered ring heterocycles.

We have selected methyl-*tert*-butylcarbodiimide as a marker for the fragmentation reactions, assuming that the cycloaddition reaction would proceed exclusively across the less hindered C=N double bond.[3] If scrambling *via* the depicted polar intermediate (Scheme I) does not occur, differentiation between the heterocyclic structures **1** and **2** is easily accomplished by nmr spectroscopy. For example, removal of the lowest boiling fractions by distillation and nmr observation could easily differentiate between MeN=C=X or *t*-BuN=C=X.

Scheme I



Results

The structures of 2 + 2 cycloadducts derived from carbodiimides and other heterocumulenes are usually assigned on the basis of spectral evidence. Exceptions are the 1,3-diazetidines **1**, X = O, obtained from isocyanates and carbodiimides, because ring-opening experiments have been used to confirm the postulated structure.[4] We had erroneously assigned the 1,3-thiazetidine structure **1**, X = S, for the 2 + 2 cycloadducts derived from isothiocyanates and carbodiimides,[5,6] and Neidlein[7] had erroneously assigned the 1,3-diazetidine structure for the 2 + 2 cycloadducts derived from benzoyl isocyanate and carbodiimides. Our present results clearly show that in the cases of isothiocyanates as well as benzoyl isocyanate addition occurs exclusively across the C=X bond (X = S or O, respectively) rather than the C=N bond.

Cycloaddition of Isocyanates to Carbodiimides. In order to check the validity of the retro 2 + 2 process we prepared the novel 2 + 2 cycloadduct **1a** from phenyl isocyanate and methyl-*tert*-butylcarbodiimide. Heating of **1a** gave rise to the exclusive formation of methyl isocyanate, phenyl-*tert*-butylcarbodiimide, and the starting materials. Since formation of *tert*-butyl isocyanate

(1) Presented in part at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 25–30, 1971.

(2) (a) H. Ulrich, B. Tucker, F. A. Stuber, and A. A. R. Sayigh, *J. Org. Chem.*, **34**, 2250 (1969); (b) R. Gompper and B. Wetzel, *Tetrahedron Lett.*, 529 (1971), have isolated a stable linear adduct of a sulfonylcarbodiimide and a ketene acetal.

(3) C. Metzger and J. Kurtz, *Chem. Ber.*, **104**, 50 (1971), observed 95% addition across the less hindered C=N double bond in the reaction of ethyl-*tert*-butylcarbodiimide with diphenylketene.

(4) W. J. Farrissey, Jr., R. J. Ricciardi, and A. A. R. Sayigh, *J. Org. Chem.*, **33**, 1913 (1968).

(5) H. Ulrich and A. A. R. Sayigh, *Angew. Chem., Int. Ed. Engl.*, **4**, 520 (1965).

(6) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

(7) R. Neidlein, *Arch. Pharm. (Weinheim)*, **297**, 623 (1964).

Table I. 1,1 Cycloadducts of Isothiocyanates and Carbodiimides[a]

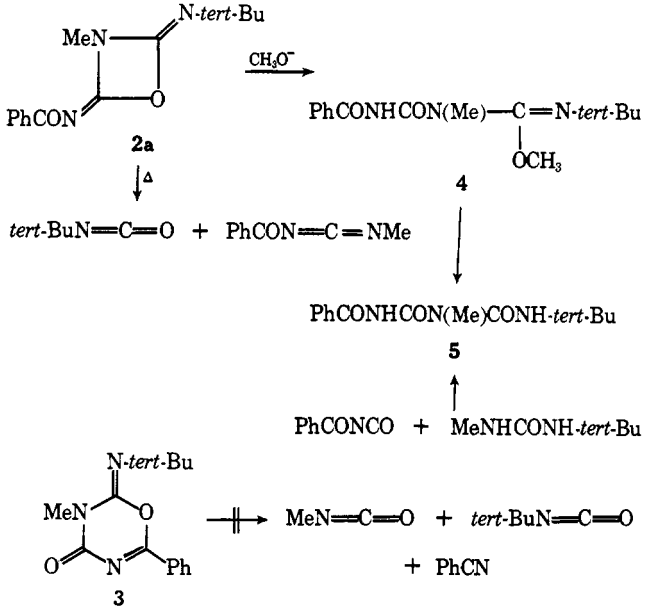
Isothiocyanate	Carbodiimide	Mp, °C	Yield[b]	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
p-Nitrophenyl	*tert*-Butylmethyl	91–92	66	$C_{13}H_{16}N_4O_3S$	53.43	5.48	19.18	53.43	5.58	18.94
p-Nitrophenyl	Diisopropyl	51–52	90.5	$C_{14}H_{18}N_4O_3S$			18.25			18.22
p-Nitrophenyl	Dicyclohexyl	73–75	95	$C_{20}H_{26}N_4O_3S$	62.14	6.77	14.52	62.19	6.85	14.33
p-Toluenesulfonyl	*tert*-Butylmethyl	87–88	61.5	$C_{14}H_{19}N_3O_3S_2$	51.69	5.67	12.92	51.52	5.88	12.79
p-Toluenesulfonyl	Diisopropyl	56–58	39.8	$C_{15}H_{21}N_3O_3S_2$	53.10	6.19	12.39	52.87	6.17	12.29
p-Toluenesulfonyl	Dicyclohexyl	152–153	81.5	$C_{21}H_{29}N_3O_3S_2$	60.14	6.92	10.02	60.64	7.01	10.25
p-Toluenesulfonyl	Diphenyl	181–182	88.5	$C_{21}H_{17}N_3O_3S_2$	61.92	4.18	10.32	62.21	4.21	10.60
p-Toluenesulfonyl	Di-*o*-tolyl	130–131	69	$C_{23}H_{21}N_3O_3S_2$	63.42	4.85	9.64	63.59	4.83	9.15

[a] The liquid cycloadducts obtained in the reaction of ethyl isothiocyanatoformate were only characterized by infrared and nmr spectroscopy. [b] The yield refers to recrystallized pure adduct; no attempts were made to optimize yields or purification.

was not observed in the fragmentation reaction, scrambling, as depicted in Scheme I, was not encountered.

The novel 2 + 2 cycloadduct derived from benzoyl isocyanate and methyl-*tert*-butylcarbodiimide was also synthesized and subjected to the fragmentation process. Heating of the relatively stable product surprisingly afforded *tert*-butyl isocyanate as the most volatile fragment, and the lower boiling methyl isocyanate was not generated at all. This result clearly indicates that the 1,3-diazetidine structure, previously assigned by Neidlein,[7] is in error, and that the 1,3-oxazetidine structure **2a** has to be considered for the 2 + 2 cycloadducts derived from benzoyl isocyanate and carbodiimides. The third possible structure **3** for the cycloadduct is also ruled out because methyl isocyanate as well as benzonitrile ought to be produced in the retro process (Scheme II).

Scheme II



Further evidence for the 1,3-oxazetidine structure **2a** was provided by mass spectral degradation and ring-opening experiments. Since **2a** is more stable than the 1,3-diazetidine derivative **1a**, loss of CH_3 from the molecular ion gives a new ion *m/e* 244, which is apparently the source of the intense ions *m/e* 160, $[PhCON{=}C{=}NMe]^+$, and *m/e* 84, $[O{\equiv}C{-}N{=}C(CH_3)_2]^+$, in the spectrum. The ring opening of **2a** with methoxide ion yields the novel pseudobiuret derivative **4**, which was hydrolyzed with dilute sodium hydroxide to produce 1-benzoyl-3-methyl-5-*tert*-butylbiuret (**5**). The latter compound was independently synthesized from benzoyl isocyanate and methyl-*tert*-butylurea (Scheme II).

The general nature of this reaction was verified by the fact that the 2 + 2 cycloadduct derived from di-*o*-tolylcarbodiimide and benzoyl isocyanate had also the 1,3-oxazetidine structure because of spectral similarity with **2a**. Interestingly, 1,3-oxazetidine derivatives are not widely known, and only a few 1,3-oxazetidin-2-ones are reported in the literature,[8] which were synthesized by cycloaddition of isocyanates to C=O double bond containing substrates.

Cycloaddition of Isothiocyanates to Carbodiimides. We observed some time ago[5,6] that reactive isothiocyanates, such as *p*-nitrophenyl, as well as alkyl and arenesulfonyl isothiocyanates, undergo a rapid reaction with carbodiimides to yield 2 + 2 cycloadducts. The four-membered ring 1,3-diazetidine structure **1**, X = S, was assigned for the cycloadducts mainly because isocyanates add to carbodiimides in this fashion. However, since it is well known that isothiocyanates add preferentially across the C=S double bond, we had indicated that the isomeric 1,3-thiazetidine structure **2**, X = S, cannot be ruled out on the basis of the spectral evidence available at that time.[9]

Fragmentation of the cycloadducts derived from methyl-*tert*-butylcarbodiimide should allow differentiation between the two possible isomeric heterocyclic structures.

Heating of the adducts derived from methyl-*tert*-butylcarbodiimide and tosyl isothiocyanate and ethyl isothiocyanatoformate, respectively, gave *tert*-butyl isothiocyanate exclusively. Likewise, heating of the adduct derived from methyl-*tert*-butylcarbodiimide and *p*-nitrophenyl isothiocyanate yielded predominantly starting materials and a minute quantity of *tert*-butyl isothiocyanate. The Feigl test for C=S double bonds[10] was found to be negative for all of the obtained 2 + 2 cycloadducts (Table I), providing further proof for the 1,3-thiazetidine structure **2**, X = S.[11]

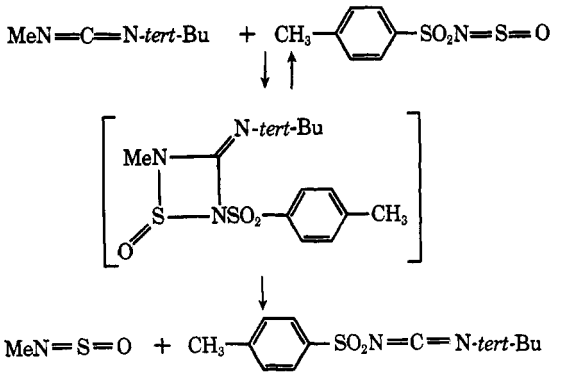
The 2 + 2 cycloadducts are obtained upon mixing of both reagents in an inert solvent or neat. Tosyl isothiocyanate and ethyl isothiocyanatoformate react more rapidly than *p*-nitrophenyl isothiocyanate, and aliphatic carbodiimides add more rapidly than aromatic carbodiimides. No reaction occurs when the reactive isothio-

(8) S. Ozaki, *Tetrahedron Lett.*, 3637 (1967); R. J. Shozda, *J. Org. Chem.*, **32**, 2960 (1967).
(9) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, Chapter V, especially p 234.
(10) W. Awe, *Pharmazie*, **3**, 492 (1948).
(11) After completion of our work I. Ojima and N. Inamoto, *J. Chem. Soc. D*, 1629 (1970), reported that isothiocyanates undergo 1,2-cycloaddition across the C=S bond.

cyanates are mixed with *p*-toluenesulfonylcyclohexylcarbodiimide.

Cycloaddition of *N*-Sulfinylsulfonamides to Carbodiimides. Aliphatic and aromatic *N*-sulfinylamines do not undergo cycloaddition to carbodiimides. However, *N*-sulfinyl-*p*-toluenesulfonamide reacts exothermically at room temperature to produce the expected exchange products. Addition of *N*-sulfinyl-*p*-toluenesulfonamide to methyl-*tert*-butylcarbodiimide resulted in the formation of *tert*-butyl-*p*-toluenesulfonylcarbodiimide and methyl-*N*-sulfinylamine (Scheme III), as

Scheme III



evidenced by infrared spectroscopy. The volatile methyl-*N*-sulfinylamine can be separated by distillation and the residual *tert*-butyl-*p*-toluenesulfonylcarbodiimide was converted to the known 1-*p*-toluenesulfonyl-3-*tert*-butylurea by addition of water to the residue.

The intermediacy of the four-membered ring compound is postulated on the basis of similarity with other heterocumulenes. However, a six-membered ring transition state could equally well accommodate the formation of the exchange products. Cram and coworkers[12] have recently shown that the exchange reaction of *N*,*N*′-bis(*p*-toluenesulfonyl)sulfur diimide and sulfoxides proceeds *via* a six-centered transition state, formed from a linear 1:1 adduct and a second sulfur diimide molecule.

Discussion

In the cycloaddition of heterocumulenes, reaction seems to occur preferentially across one of the double bonds. Since both reagents can function as either electron donors or electron acceptors, it is not clear what function each particular heterocumulene molecule has in the respective cycloaddition reactions. Trapping of a zwitterionic intermediate by a 1,4-dipolar cycloaddition could shed some light on this question. Even if we deal with concerted stereospecific processes, a stepwise reaction sequence is a rational assumption. However, such intermediates have rarely been trapped. We have isolated 1,4-dipolar cycloadducts in the reaction of arenesulfonyl isocycanates with carbodiimides, indicating that the carbodiimide functions as the electron donor and arenesulfonyl isocyanates as well as arenesulfonylcarbodiimides act as electron acceptors. Such initial reaction, of course, could produce both heterocyclic isomers (as shown in Scheme I). If we assume that the initial bond formation in the case of aroyl isocyanates and the isothiocyanates under discussion occurs by donation of a pair of electrons from oxygen or sulfur, respectively, to the electrophilic center carbon atom in the carbodiimides, the observed products could only be formed. Although such an argument would explain the exclusive formation of the observed products nicely, it is necessary to verify this pathway by trapping experiments. However, initial electron donation of the carbodiimide seems to be more likely, and the generated dipolar intermediate could undergo subsequent closure to the thermodynamically most stable product.

The symmetry of the four-membered ring allows the ready exchange of substituents on heterocumulenes, and it has been assumed that equilibria with the starting materials and the new set of heterocumulenes are established.[13] However, our results clearly show that a reverse reaction involving the new set of heterocumulenes does not occur if one of the new products is an alkyl derivative. The exchange reaction therefore allows a very clean transformation of one set of heterocumulenes into a new set of heterocumulenes, which is of preparative significance.

Experimental Section

Melting and boiling points are uncorrected. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ir spectra were determined using a Beckman IR-8 spectrophotometer. Nmr spectra were obtained from samples in $CDCl_3$ or CCl_4 solutions with a Varian T-60 instrument using tetramethylsilane as the internal standard.

Methyl-*tert*-butylcarbodiimide. To 204.4 g (1.4 mol) of methyl-*tert*-butylthiourea (prepared from *tert*-butylamine and methyl isothiocyanate in 89% yield) in 600 ml of methylene chloride, dropwise and with cooling, 153 g (1.54 mol) of carbonyl chloride, collected in 300 ml of methylene chloride, was added at 2–8° over a period of 75 min. The reaction mixture was refluxed for 90 min while excess phosgene was removed with nitrogen. The reaction mixture was added dropwise and with cooling over a period of 1 hr to 132 g (3.3 mol) of sodium hydroxide dissolved in 1300 ml of water, and the organic layer was separated and dried with $MgSO_4$. Distillation yielded 102.4 g (65.3%) of methyl-*tert*-butylcarbodiimide, bp 124–125° (760 mm) [lit.[14] bp 119.5–120.5° (707 mm)].

1-Methyl-3-phenyl-4-(*tert*-butylimino)-2-uretidinone (1a). To 11.2 g (0.1 mol) of methyl-*tert*-butylcarbodiimide, dropwise and with stirring, 11.9 g (0.1 mol) of phenyl isocyanate was added. An exothermic reaction was observed, and the solid cycloadduct was dissolved in ligroine and crystallized upon cooling in a Dry Ice–acetone bath, yielding 10.5 g (45.4%) of 1-methyl-3-phenyl-4-(*tert*-butylimino)-2-uretidinone: mp 52°; ir ($CHCl_3$) 1709 cm^{-2} (C=O); nmr ($CDCl_3$) δ 1.48 (s, 9, $(CH_3)_3C$), 3.03 (s, 3, CH_3), 7.28 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 231 (18), 174 (15.5), 159 (3.5), 146 (3.5), 132 (35), 119 (52), 112 (51), 97 (100), 91 (26), 83 (31), 77 (20), 57 (52).

Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.53; H, 7.36; N, 18.18. Found: C, 67.58; H, 7.36; N, 18.17.

Thermolysis. An amount of 9.2 g (0.04 mol) of the cycloadduct was heated in an oil bath and 1.75 g (76.8%) of methyl isocyanate, bp 37–39°, was removed by distillation. Vacuum distillation of the residue yielded 4.8 g (69%) of *tert*-butylphenylcarbodiimide, bp 56° (0.005 mm).[15]

2-Benzoylimino-3-methyl-1,3-oxazetidine-4-*tert*-butylimine (2a). To 11.5 g (0.1 mol) of methyl-*tert*-butylcarbodiimide, dropwise and with stirring, 15.1 g (0.1 mol) of benzoyl isocyanate was added. An immediate exothermic reaction was noted and the temperature rose to 110°. The cycloadduct crystallized on cooling, and trituration with ligroine gave 21.5 g (80.8%) of 2-benzoylimino-3-methyl-1,3-oxazetidine-4-*tert*-butylimine: mp 114–115° after recrystallization from isopropyl alcohol; ir ($CHCl_3$) 1689, 1634

(12) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970).

(13) W. Neumann and P. Fischer, *Angew. Chem., Int. Ed. Engl.*, **1**, 621 (1962).

(14) E. Schmidt, W. Striewsky, and F. Hirtzler, *Justus Liebigs Ann. Chem.*, **560**, 222 (1948).

(15) P. Schlack and G. Keil, *ibid.*, **661**, 164 (1963).

cm^{-1}; nmr ($CDCl_3$) δ 1.4 (s, 9, $(CH_3)_3C$), 3.32 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 259 (25), 244 (100), 187 (30), 160 (5), 147 (42), 141 (44), 122 (11), 112 (17), 105 (94), 97 (82), 84 (69), 77 (94), 57 (85).

Anal. Calcd for $C_{14}H_{17}N_3O_2$: C, 64.86; H, 6.56; N, 16.22. Found: C, 64.58; H, 6.69; N, 16.14.

Thermolysis. An amount of 2.6 g of the cycloadduct was dissolved in 10 ml of chlorobenzene, and most of the chlorobenzene was removed by distillation (bath temperature to 180°). The distilled chlorobenzene contained a mixture of *tert*-butyl isocyanate (ir N=C=O at 2275 cm^{-1}; nmr δ 1.1 (s, 9, $(CH_3)_3C$)), and methyl-*tert*-butylcarbodiimide (ir N=C=N at 2130 cm^{-1}; nmr δ 1.02 (s, 9, $(CH_3)_3C$), 2.5 (s, 3, CH_3)).

Hydrolysis. A. Phenoxide in Methanol. To a solution of 7.77 g (0.3 mol) of the cycloadduct in 200 ml of methanol, 0.2 g of sodium phenoxide was added and the mixture was refluxed for 45 min. Evaporation of the methanol gave a residue which was redissolved in diethyl ether to remove the sodium phenoxide catalyst; evaporation and reprecipitation of the residue from methanol–water gave 5.9 g (67.6%) of **1-benzoyl-3-methyl-4-methyl-5-*tert*-butylpseudobiuret (4)**: mp 80–81°; ir ($CHCl_3$) 1709–1626 cm^{-1}; nmr ($CDCl_3$) δ 1.38 (s, 9, $(CH_3)_3C$), 3.12 (s, 3, CH_3N), 3.94 (s, 3, CH_3O).

Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 61.86; H, 7.22; N, 14.43. Found: C, 62.07; H, 7.44; N, 14.54.

B. Phenoxide in Acetone–Water. To a solution of 2 g of the cycloadduct in a mixture of 50 ml of water and 30 ml of acetone an amount of 0.05 g of sodium phenoxide was added, and after refluxing for 1 hr and cooling, 0.72 g (34%) of **1-benzoyl-3-methyl-5-*tert*-butylbiuret (5)** was collected by filtration: mp 178–179° after recrystallization from methanol; ir ($CHCl_3$) 1748, 1653 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.4 (s, 9, $(CH_3)_3C$), 3.25 (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{19}N_3O_3$: C, 60.63; H, 6.91; N, 15.15. Found: C, 60.53; H, 7.00; N, 15.25.

1-Benzoyl-3-methyl-5-*tert*-butylbiuret (5). To a suspension of 3.9 g (0.03 mol) of methyl-*tert*-butylurea in 120 ml of ethylene dichloride, dropwise and with stirring, 4.41 g (0.03 mol) of benzoyl isocyanate was added. Filtration yielded 5 g (60.2%) of 1-benzoyl-3-methyl-5-*tert*-butylbiuret, mp 177–178°, identical with the compound obtained by aqueous hydrolysis of 2-benzoylimino-3-methyl-1,3-oxazetidine-4-*tert*-butylimine.

2-Benzoylimino-3-*o*-tolyl-1,3-oxazetidine-4-*o*-tolylimine. To 4.4 g (0.02 mol) of di-*o*-tolylcarbodiimide an amount of 2.94 g (0.02 mol) of benzoyl isocyanate was added dropwise. After standing overnight the reaction mixture solidified, and a crude solid product was obtained, which was recrystallized from methanol to yield 2.5 g (34%) of light yellow crystals of 2-benzoylimino-3-*o*-tolyl-1,3-oxazetidine 4-*o*-tolylimine: mp 178–179°; ir ($CHCl_3$) 1689, 1634 cm^{-1}

Anal. Calcd for $C_{22}H_{19}N_3O_2$: C, 74.79; H, 5.15; N, 11.37. Found: C, 74.27; H, 5.11; N, 11.03.

2-(*p*-Toluenesulfonylimino)-3-methyl-1,3-thiazetidine-4-*tert*-butylimine (2b). General Procedure. The preparation of 2-(*p*-toluenesulfonylimino)-3-methyl-1,3-thiazetidine-4-*tert*-butylimine exemplifies the procedure followed in the preparation of the 1,3-thiazetidines listed in Table I with the exception of compounds $C_{13}H_{16}N_4O_2S$ and $C_{21}H_{29}N_3O_2S_2$ which were obtained from a 10% solution in benzene. To 2.24 g (0.02 mol) of methyl-*tert*-butylcarbodiimide an amount of 4.26 g (0.02 mol) of tosyl isothiocyanate was added. An immediate exothermic reaction was observed and after cooling to room temperature the reaction mixture was dissolved in isopropyl alcohol and the crude cycloadduct was precipitated with water. Recrystallization from isopropyl alcohol gave 4 g (61.5%) of white crystals, mp 87–88°.

Thermolysis. Heating of 2 g of the cycloadduct in an oil bath to 160° under a slight vacuum resulted in distillation of 0.48 g (68.6%) of *tert*-butyl isothiocyanate, which was identified by nmr spectroscopy (singlet at δ 1.4 ppm). Short refluxing of a 10% solution in *o*-dichlorobenzene and ir examination verified the formation of *p*-toluenesulfonylcyclohexylcarbodiimide by the characteristic $-SO_2N=C=N-$ band at 2175 cm^{-1}.

Reaction of Methyl-*tert*-butylcarbodiimide with Ethyl Isothiocyanatoformate. To 4.48 g (0.04 mol) of methyl-*tert*-butylcarbodiimide, dropwise with stirring and cooling, 5.24 g (0.04 mol) of ethyl isothiocyanatoformate was added, and the formation of the cycloadduct was indicated by the disappearance of the heterocumulene bands and the appearance of new bands in the 1653–1587-cm^{-1} region. A 4-g (0.016 mol) sample of the cycloadduct was heated in an oil bath to 190° with simultaneous removal of 1.5 g (79%) of *tert*-butyl isothiocyanate: bp 140°; $\lambda_{max}^{CHCl_3}$ 2041 cm^{-1}; nmr ($CDCl_3$) δ 1.42 (s, 9, $(CH_3)_3C$).

Reaction of Methyl-*tert*-butylcarbodiimide with *N*-Sulfinyl-*p*-toluenesulfonamide. To 2.24 g (0.02 mol) of methyl-*tert*-butylcarbodiimide, dropwise and with stirring, 4.34 g (0.02 mol) of *N*-sulfinyl-*p*-toluenesulfonamide was added. An exothermic reaction was observed and the formation of *tert*-butyl-*p*-toluenesulfonylcarbodiimide was indicated by ir spectroscopy ($-SO_2N=C=N$ at 2175 cm^{-1}). An amount of 0.8 g (64.5%) of methyl-*N*-sulfinylamine, bp 58–59°, nmr ($CDCl_3$) δ 3.6 (s, 3, CH_3), was removed by distillation, and addition of water to the residue yielded 0.8 g of 1-*p*-toluenesulfonyl-3-*tert*-butylurea, mp 168–170° (lit.[16] mp 167–168°).

Acknowledgment. The authors wish to express their appreciation to P. A. Meulman and L. Baczynskyj, The Upjohn Co., Physical and Analytical Chemistry Section, Kalamazoo, Mich., for the mass spectral data.

(16) H. Ruschig, G. Korger, W. Aumüller, H. Wagner, J. Scholz, and A. Baender, German Patent 974,062 (1960); *Chem. Abstr.*, **56**, 4679 (1962).