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# Preparations and Reactions of *N*-Benzoyl- and *N*-Ethoxycarbonylcarbodiimides

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The reaction of *N*-benzoyl-*N'*-*t*-butylthiourea with either diethyl azodicarboxylate or azodibenzoyl resulted in the formation of benzoyl-*t*-butylcarbodiimide in 84% and 48% yields, respectively. Dehydrosulfurization of various thioureas was also effected with mercuribenzamide. Benzoyl- or ethoxycarbonylcarbodiimides were obtained in over 80% yields. The reaction of benzoyl-*t*-butylcarbodiimide with one equivalent each of *N*-benzoylglycine and glycine ethyl ester led to the formation of $N^1$-benzoyl-$N^2$-*t*-butyl-$N^3$-(ethoxycarbonyl)methylguanidine in a good yield, no *N*-benzoylglycylglycine ethyl ester being isolated. When benzoyl-*t*-butylcarbodiimide was allowed to react with benzoic acid, dibenzimide and *t*-butyl isocyanate were formed. Similarly, *N*-ethoxycarbonylbenzamide and *N*-benzoylglycine(*N'*-ethoxycarbonyl)amide were prepared in good yields.

Carbodiimides have been used as versatile reagents in organic synthesis. For the preparation of peptides and nucleotides, dicyclohexylcarbodiimide (DCC) has been extensively used.[1] The reactivity of DCC, however, decreases in the presence of strong bases.[2] Thus, it is desirable to prepare more reactive carbodiimides such as *N*-acylcarbodiimides. $\alpha,\beta$-Unsaturated carbonyl compounds undergo base catalyzed addition (Michael reaction)[3] and *N*-acylcarbodiimides are expected to show a similar reaction.

Some *N*-acyl-, *N*-ethoxycarbonyl- and *N*-sulfonylcarbodiimides have been synthesized but with low

1) a) H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953): b) F. Kurzer and K. Douraghi-Zadeh, *ibid.*, **67**, 107 (1967): c) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," John Wiley & Sons, Inc., (1961): d) P. T. Gilham and H. G. Khorana, *J. Amer. Chem. Soc.*, **80**, 6212 (1958): e) K. L. Agarwal, A. Yamazaki, and H. G. Khorana, *ibid.*, **93**, 2754 (1971).

2) a) H. Schaller and H. G. Khorana, *ibid.*, **85** 3828 (1963). b) T. M. Jacob and H. G. Khorana, *ibid.*, **86**, 1630 (1964). c) R. Lohrmann and H. G. Khorana, *ibid.*, **86**, 4188 (1964). d) R. K. Ralph, W. J. Connors, H. Schaller, and H. G. Khorana, *ibid.*, **85**, 1983 (1963).

3) E. D. Bermann, D. Ginsburg, and R. Pappo, "Organic Reactions," Vol. 10, John Wiley & Sons, Inc. (1959), p 179.

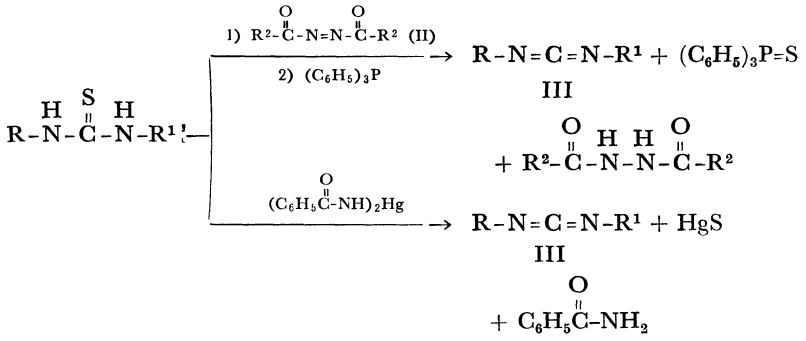
yields.[4] In this report we present convenient methods for the preparation of *N*-benzoyl- and *N*-ethoxycarbonylcarbodiimides and some reactions of the carbodiimides.

*Preparation of* N-*Benzoylcarbodiimides by Means of either Diethyl Azodicarboxylate or Azodibenzoyl and Triphenylphosphine.* The reaction of *N*, *N'*-disubstituted thioureas (I) with diethyl azodicarboxylate (IIa) followed by treatment with triphenylphosphine resulted in the formation of the corresponding disubstituted carbodiimides in good yields.[5] Since the reaction proceeds in a neutral medium without any formation of reactive compounds such as water or strong acids, the process might be applied to preparation of more reactive carbodiimides.

When *N*-benzoyl-*N'*-*t*-butylthiourea (Ie) was allowed to react with an equimolar amount of IIa in tetrahydrofuran(THF) at room temperature, orange red of IIa faded in 3 days. After treatment with triphenylphosphine, benzoyl-*t*-butylcarbodiimide (IIIe), diethyl hydrazodicarboxylate and triphenylphosphine sulfide were obtained in 84%, 79%, and 71% yields, respectively.

We might assume that the reactivity of azo compounds depends on electron affinity of the nitrogen-nitrogen double bond. Thus, azodibenzoyl (IIb) was used in place of IIa in the above reaction.

The reaction of Ia, Ib, or Id with IIb in THF at room temperature led to the formation of the corresponding carbodiimide (IIIa, IIIb, or IIId) and *N,N'*-dibenzoylhydrazine in nearly quantitative yields. Thin layer chromatography (tlc) of the reaction mixture revealed the presence of sulfur. Unlike the reaction of I with IIa,[5] no 1 : 1 adduct of I with IIb could be isolated. When *N*-benzoyl-*N'*-*t*-butylthiourea (Ie) was treated with an equimolar amount of IIb at room temperature, the orange red of IIb disappeared within 4 hr and IIIe was isolated in a 47% yield. In order to facilitate the purification of the carbodiimide, an equimolar amount of triphenylphosphine was added before working up. An attempt to isolate benzoylcyclohexylcarbodiimide (IIIf) by distillation, however, was unsuccessful, presumably due to limited stability against moisture. Thus, the reaction mixture resulting from the reaction of *N*-benzoyl-*N'*-cyclohexylthiourea (If) with IIb was treated with water and *N*-benzoyl-




I, III a : $R=R^1=C_6H_5-$ d : $R=R^1=cyclo\text{-}C_6H_{11}-$ g : $R=C_2H_5OCO-$, $R^1=t\text{-}C_4H_9-$
b : $R=R^1=p\text{-}CH_3OC_6H_4-$ e : $R=C_6H_5CO-$, $R^1=t\text{-}C_4H_9$ h : $R=C_2H_5OCO-$, $R^1=cyclo\text{-}C_6H_{11}-$
c : $R=R^1=p\text{-}CH_3C_6H_4-$ f : $R=C_6H_5CO-$, $R^1=cyclo\text{-}C_6H_{11}-$
II a : $R^2=C_2H_5O-$ b : $R^2=C_6H_5-$

Table 1. Preparation of *N*-benzoyl- and *N*-carboethoxycarbodiimides from thioureas

| Method[a] | R-N=C=N-R' R | R' | Yield % | Bp°C (mmHg) | IR ($\nu$ cm$^{-1}$) -N=C=N- | C=O |
|---|---|---|---|---|---|---|
| A | $C_6H_5CO-$ | $t\text{-}C_4H_9-$ | 48 | 72—74 (0.08) | 2150 | 1660 |
| A' | | | 84 | 110 (0.55) | | |
| B | | | 88 | 98 (0.2) | | |
| A | $C_6H_5CO-$ | $cyclo\text{-}C_6H_{11}-$ | 46[b] | | 2150 | 1687 |
| B | | | 82[b] | | | |
| B | $C_2H_5OCO-$ | $t\text{-}C_4H_9-$ | 88 | 57—58 (0.35) | 2150 | 1730 |
| B | $C_2H_5OCO-$ | $cyclo\text{-}C_6H_{11}-$ | 86 | 83—86 (0.01) | 2150 | 1725 |

a) A; Reaction with azodibenzoyl and triphenylphosphine. A'; Reaction with diethyl azodicarboxylate and triphenylphosphine. B; Reaction with mercuribenzamide.
b) Yield of *N'*-benzoyl-*N'*-cyclohexylurea obtained by treatment of the reaction mixture with water.

4) a) H. Ulrich and A. A. R. Sayigh, *Angew. Chem.*, **76**, 781 (1964): b) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966): c) R. Neidlein and E. Heukelbach, *Tetrahedron Lett.*, **1965**, 149: d) R. Neidlein and E. Heukelbach, *Arch. Pharm.*, **299**, 709 (1966), *Chem. Abstr.*, **66**, 37600j (1967): e) Larbwerke Hoechst A. -G., Ger. 1240519; *Chem. Abstr.*, **67**, 73181c (1967): f) Chemische Fabrik von Heyden A. -G., Neth. Appl., 6610608; *Chem. Abstr.*, **67**, 90554u (1967): g) J. Goerdeler, H. Lohmann, R. Losch, and S. Raddatz, *Tetrahdron Lett.*, **1971**, 2765.

5) a) O. Mitsunobu, K. Kato, and F. Kakese, *ibid.*, **1969**, 2473: b) O. Mitsunobu, K. Kato, and M. Tomari, *Tetrahedron*, **26**, 5731 (1970).

*N'*-cyclohexylurea was obtained in a 46% yield.

*Preparation of Disubstituted Carbodiimides by Means of Mercuribenzamide.* The above reaction is coupled to a redox system, *i. e.*, the hydrogen atoms in thiourea are abstracted by azo compounds and the sulfur atom in it is eliminated by the formation of triphenylphosphine sulfide. Other reagents capable of abstracting hydrogen and sulfur atoms may therefore be used for the preparation of carbodiimides. Mercuribenzamide (IV) was chosen for this purpose.

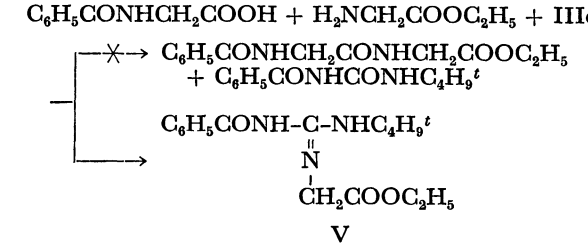
Mercuribenzamide was allowed to react with an equimolar amount of Ia, Ic, or Id in benzene at room temperature for 2 hr. After removal of mercuric sulfide, IIIa, IIIc, or IIId was obtained in nearly quantitative yields.

Similarly, some *N*-benzoyl- and *N*-ethoxycarbonylcarbodiimides (IIIe—h) were prepared in over 80% yields. The results are summarized in Table 1.

*Reaction of* N-*Benzoyl*-N'-t-*butylcarbodiimide and* N-*Ethoxycarbonyl*-N'-t-*butylcarbodiimide.* A special merit asociated with the use of DCC in the preparation of peptides is ease in manipulation. However, under certain conditions, *O*-acylisoureas initially formed from DCC and *N*-protected amino acids exhibit a marked propensity to undergo ready rearrangement of the acyl group giving *N*-acylureas.[1c]

The reaction of IIIe with an *N*-protected amino acid may also lead to the formation of corresponding *O*-acylisourea, in which the electron density of the nitrogen atom having a benzoyl group is reduced and another nitrogen atom is crowded by *t*-butyl group. Thus we might expect that the rearrangement to an *N*-acylurea *via* acyl transfer is prevented.

The reaction of IIIe with one equivalent each of *N*-benzoylglycine and glycine ethyl ester in dichloromethane at room temperature unexpectedly resulted in the formation of $N^1$-benzoyl-$N^2$-*t*-butyl-$N^3$-ethoxycarbonylmethylguanidine (V) in a 76% yield, 77% of *N*-benzoylglycine being recovered. *N*-Benzoyl-*N'*-*t*-butylurea was obtained in an 18% yield, but no *N*-benzoylglycylglycine ethyl ester was isolated. Similarly, V was prepared in a 71% yield when the reaction was carried out in THF.




In general, DCC reacts with the carboxyl function of amino acids even when both amine and carboxylic acid reactants exist. Thus, the reactivity of IIIe is quite different from that of DCC and closely resembles that of isocyanates.

The reaction of IIIe with benzoic acid was attempted in order to test its reaction with carboxylic acid. Benzoic acid was allowed to react with an equimolar amount of IIIe in dichloromethane at room temperature

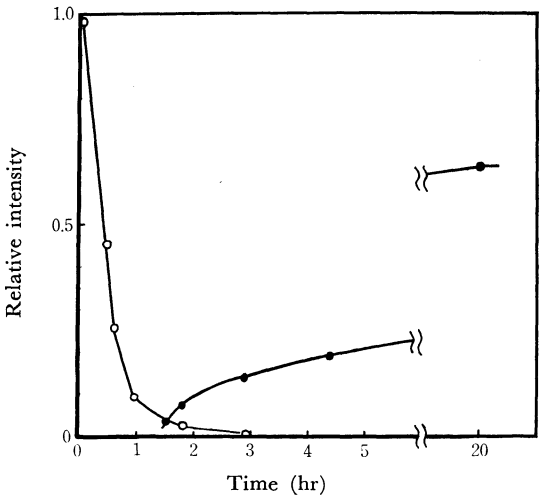
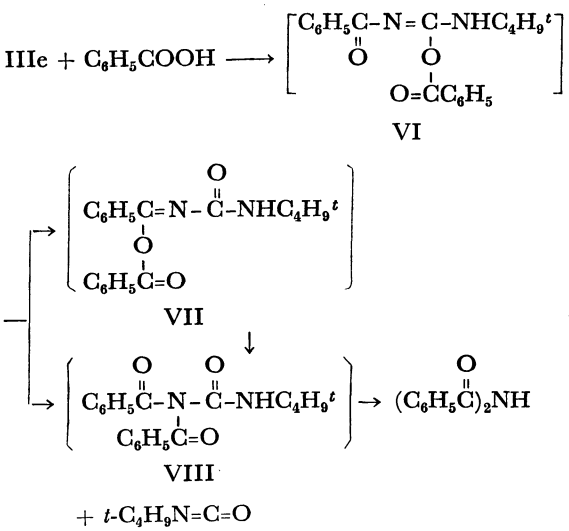



Fig. 1. Relative intensity of absorptions at 2150 and 2250 $cm^{-1}$.
—○— : Absorption at 2150 $cm^{-1}$
—●— : Absorption at 2250 $cm^{-1}$

and the reaction was followed by IR spectrum. The absorption at 2150 $cm^{-1}$ attributed to the –N=C=N– bond virtually disappeared in 2 hr, and a new absorption at 2250 $cm^{-1}$ appeared in 1.5 hr. Intensity of the new absorption became constant after 20 hr and dibenzimide was isolated in a 72% yield from the reaction mixture (Fig. 1). When IIIe was allowed to react with benzoic acid for 20 hr followed by treatment with aniline, *N*-phenyl-*N'*-*t*-butylurea was obtained in an 87% yield. This unexpected result may be explained as follows: *O*-benzoyl-isourea (VI) formed from IIIe and benzoic acid is converted into *N*-dibenzoyl-*N'*-*t*-butylurea (VIII). VIII subsequently is decomposed to dibenzimide and *t*-butyl isocyanate by intramolecular hydrogen transfer. The possibility of initial formation of an imidoyl benzoate (VII) prior to VIII could not be ruled out.




That the transfer of the benzoyl group took place rapidly was proved by the following experiment. When IIIe was treated with benzoic acid for 2 hr at room temperature and then aniline was added, benzanilide was obtained only in a 33% yield along with *N*-benzoyl-

*N'-t*-butylurea, *N*-phenyl-*N'-t*-butylurea, and benzamide.

When the reaction of IIIe with benzoic acid was carried out in the presence of a catalytic amount of triethylamine and the reaction was followed by IR spectrum as above, it took over 5 hr for the carbodiimide to disappear. On the other hand, a new absorption at 2250 $cm^{-1}$ appeared in 30 min.

Similarly, the reaction of ethoxycarbonyl-*t*-butylcarbodiimide (IIIg) with an equimolar amount of benzoic acid or *N*-benzoylglycine resulted in the formation of *N*-ethoxycarbonylbenzamide and *N*-benzoylglycine(*N'*-ethoxycarbonyl)amide in fairly good yields.

$$C_2H_5O-\overset{O}{\overset{\|}{C}}-N=C=N-C_4H_9^t + R-COOH$$

IIIg

$$\rightarrow C_2H_5O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-R + t\text{-}C_4H_9N=C=O$$

$R = C_6H_5-$ or $C_6H_5CONHCH_2-$

## Experimental

The IR spectra were measured on a Nippon Bunko IR-G spectrophotometer. The NMR spectra were obtained on a Hitachi Perkin-Elmer R-20 high resolution spectrometer at 60 MHz, using tetramethylsilane as an internal standard. Thin layer chromatography (tlc) was carried out on Merck $PF_{254}$ or Wako Gel B-5.

*Reagents.* Diethyl azodicarboxylate,[6] azodibenzoyl,[7] and mercuribenzamide[8] were prepared by the usual procedures. *N*-Benzoyl- and *N*-ethoxycarbonyl thioureas were prepared from an amine and either benzoyl or ethoxycarbonyl thioisocyanate. The solvents were purified by ordinary procedures.

*Preparation of Benzoyl-t-butylcarbodiimide by the Reaction of N-Benzoyl-N'-t-butylthiourea with an Azo Compound and Triphenylphosphine.* *a) Using Diethyl Azodicarboxylate.* A solution of diethyl azodicarboxylate (1.74 g, 10 mmol) in THF (3 m*l*) was added dropwise to a solution of *N*-benzoyl-*N'-t*-butylthiourea (2.36 g, 10 mmol) in THF (10 m*l*) with stirring at room temperature. After the solution was kept standing at room temperature for 2 days, triphenylphosphine (2.62 g, 10 mmol) in THF (6 m*l*) was added, The solution was stirred for 1 hr and concentrated *in vacuo*. The residue was extracted with petroleum ether (30—60°C) to separate soluble material from the remainder. The extract was concentrated and distilled to give benzoyl-*t*-butylcarbodiimide, bp 110°C/0.55 mmHg, 1.65 g (84%), IR (neat): 2150 (-N=C=N-) and 1660 $cm^{-1}$ (>C=O). NMR ($CCl_4$): $\delta$ 1.40 (s, 9H, $-C(CH_3)_3$), 7.30 and 7.90 (m, 3H and 2H, aromatic protons). The material, insoluble in petroleum ether, was applied to a column (2.5×25 cm) of alumina in benzene. The column was eluted first with benzene and then with methanol. Triphenyl phosphine sulfide (71%) was obtained from the benzene fraction and diethyl hydrazodicarboxylate (79%) was obtained from the methanol fraction.

*b) Using Azodibenzoyl.* A solution of azodibenzoyl (1.19 g, 5 mmol) in benzene (35 m*l*) was added dropwise to a solution of *N*-benzoyl-*N'-t*-butylthiourea (1.18 g, 5 mmol) in benzene with stirring at room temperature. After the mixture was stirred for 5 hr, dibenzoylhydrazine (mp 245—248°C, 1.12 g, 93%) was filtered off. Triphenylphosphine (1.31 g, 5 mmol) in benzene (10 m*l*) was then added to the filtrate and a white precipitate formed was removed by filtration. The filtrate was concentrated *in vacuo* and the residue was extracted with petroleum ether (30—60°C) to separate soluble material from the remainder. The extract was concentrated and distilled to give IIIe, bp 71—74°C/0.08 mmHg, 482 mg (48%). The material, insoluble in petroleum ether, was triphenylphosphine sulfide, mp 155—162°C, 1.14 g (78%).

*Reaction of N-Benzoyl-N'-cyclohexylthiourea with Azodibenzoyl.* A solution of IIb (238 mg, 1 mmol) in benzene (1 m*l*) was added dropwise to a solution of **If** (262 mg, 1 mmol) in benzene (2 m*l*) with stirring at room temperature. After the mixture was stirred for 4 hr, dibenzoylhydrazine (mp 244—245°C, 195 mg, 81%) was removed by filtration. The IR spectrum of the filtrate showed strong absorption at 2150 $cm^{-1}$ (-N=C=N-). The filtrate was treated with water (1 m*l*), the product being separated by preparative tlc (dichloromethane, benzene-THF (1 : 1), and benzene) to give sulfur (20 mg, 63%) and *N*-benzoyl-*N'*-cyclohexylurea, mp 161—162°C, 57 mg (46%). IR (KBr): 3250 (>N-H), 1690 (>C=O), and 1600 $cm^{-1}$ ($C_6H_5-$). NMR ($CCl_4$): $\delta$ 1.8 (m, 11H, *cyclo*-$C_6H_{11}-$), 3.75 (broad s, 1H, >N-H), 7.5 and 8.15 (m, 3H and 2H, aromatic protons), and 9.0 (1H, >N-H).

*Preparation of N-Benzoyl- and N-Ethoxycarbonylcarbodiimides from Thioureas and Mercuribenzamide.* Equimolar amounts (20 mmol) of *N*-benzoyl- or *N*-ethoxycarbonylthiourea (I) and IV were suspended in benzene (100 m*l*) and the mixture was stirred for 3 hr at room temperature. After mercuric sulfide was removed by filtration, the filtrate was evaporated and the residue was extracted with petroleum ether. The corresponding carbodiimide was obtained by distillation from the extracts. The results are summarized in Table 1.

*Reaction of N-Benzoyl-N'-t-butylcarbodiimide with N-Benzoylglycine and Glycine Ethyl Ester.* A suspension of *N*-benzoylglycine (179 mg, 1 mmol) and IIIe (202 mg, 1 mmol) in dichloromethane (6 m*l*) was stirred for 20 min at room temperature. A solution of glycine ethyl ester (103 mg, 1 mmol) in dichloromethane was then added dropwise in 20 min to the suspension. After the mixture was kept standing overnight, *N*-benzoylglycine was separated by filtration, mp 187—191°C, 137 mg (77%). The filtrate was applied to silica gel plates which were developed in chloroform. The main band was further separated by tlc (ether) giving *N*-benzoyl-*N'-t*-butylurea, 40 mg, 18%, mp 144—145°C (from ethanol): Found: C, 65.46; H, 7.34%. Calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32%. NMR ($CCl_4$): $\delta$ 1.5 (s, 9H, $-C(CH_3)_3$), 7.4—8.15 (m, 5H, aromatic protons), 9.1 (1H, >N-H), and 10.9 (1H, >N-H), and $N^1$-benzoyl-$N^2$-*t*-butyl-$N^3$-carboethoxymethylguanidine (232 mg, 76%, mp 96—98°C (from petroleum ether). Found: C, 62.98; H, 7.59; N, 13.74%. Calcd for $C_{16}H_{23}N_3O_3$: C, 62.93; H, 7.59; N, 13.76%. IR (KBr): 1750 $cm^{-1}$ (>C=O). NMR ($CCl_4$): $\delta$ 1.25 (t, 3H, $-O-\overset{|}{C}-CH_3$), 1.5 (s, 9H, $-C(CH_3)_3$), 2.5 (1H, >N-H), 4.25 (m, 4H, $>NCH_2CO_2CH_2\overset{|}{C}-$), 7.4 and 8.15 (m, 5H, aromatic protons), and 10.4 (1H, >N-H).

When the reaction was carried out in THF, the guanidine was obtained in a 71% (215 mg) yield.

*Reaction of N-Benzoyl-N'-t-butylcarbodiimide with Aniline.* A solution of aniline (93 mg, 1 mmol) in dichloromethane (1.5 m*l*) was added dropwise to a solution of IIIe (202 mg, 1 mmol) in dichloromethane (1.5 m*l*) with stirring at room temperature. After about 1 hr, the tlc of the solution re-

6) N. Rabjohn, "Organic Syntheses," Coll. Vol. III, p 375 (1955).
7) H. Bock and J. Kroner, *Chem. Ber.*, **99**, 2039 (1966).
8) J. W. Williams, W. T. Rainey, Jr., and R. S. Leopold, *J. Amer. Chem. Soc.*, **64**, 1738 (1942).

vealed a new spot while no starting materials remained. The solution was kept standing overnight and the solvent was removed under reduced pressure giving $N^1$-benzoyl-$N^2$-*t*-butyl-$N^3$-phenylguanidine, mp 100—101°C, 286 mg (97%). The guanidine was recrystallized from petroleum ether, mp 102°C. NMR ($CCl_4$): $\delta$ 1.5 (s, 9H, $-C(CH_3)_3$), 4.8 (1H, >N–H), 7.25 and 8.15 (m, 10H, aromatic protones), and 12.4 (1H, >N–H).

*Reaction of Benzoyl-t-butylcarbodiimide with Benzoic Acid. a) Measurement of IR Spectrum of the Reaction Mixture.* A solution of IIIe (202 mg, 1 mmol) and benzoic acid (122 mg, 1 mmol) in dichloromethane (3 m*l*) was placed in 0.05 cm matched cell (NaCl) and the reaction was followed by means of IR spectrum at room temperature. Figure 1 shows relative intensity of absorption at 2150 and 2250 $cm^{-1}$.

*b) Treatment of the Reaction Mixture with Aniline.* A solution of IIIe (202 mg, 1 mmol) and benzoic acid (122 mg, 1 mmol) in dichloromethane (4.5 m*l*) was stirred at room temperature for 2 hr. Aniline (93 mg, 1 mmol) in dichloromethane (3 m*l*) was then added and the solution was stirred for additional 5 hr. After the solution was kept standing overnight, the products were isolated by preparative tlc (1,2-dichloroethane–ether (30 : 1) and 1,2-dichloroethane–ether (15 : 1)) giving benzanilide (mp 163—164°C, 64 mg, 33%), *N*-benzoyl-*N'*-*t*-butylurea (mp 140—142°C), *N*-phenyl-*N'*-*t*-butylurea (mp 164—165°C) and benzamide.

In a separate experiment in which the mixture obtained as above was stirred for 20 hr, followed by treatment with aniline (93 mg, 1 mmol) in dichloromethane (3 m*l*), benzanilide (mp 162—163°C, 44 mg, 22%), benzamide (mp 127—128°C, 23 mg, 19%) and *N*-phenyl-*N'*-*t*-butylurea (mp 166—168°C, 167 mg, 87%) were obtained.

*c) Treatment of the Reaction Mixture with Water.* A mixture obtained as above was stirred for 20 hr at room temperature followed by addition of water (0.1 m*l*). After the solution was kept standing overnight, dibenzimide was obtained by preparative tlc using dichloromethane–ether (10 : 1) in a 72% yield, mp 150—151°C (from ethanol–water, 1 : 1). Satisfactory analytical and spectra data were obtained.

*Reaction of* N-*Ethoxycarbonyl*-N'-t-*butylcarbodiimide with Benzoic Acid.* A solution of IIIg (85 mg, 0.5 mmol) and benzoic acid (61 mg, 0.5 mmol) in THF (1.5 m*l*) was refluxed for 3.5 hr and kept standing overnight. After removal of the solvent under reduced pressure, a quantitative amount of *N*-ethoxycarbonylbenzamide (mp 108—109°C) was obtained which was recrystallized from ethanol, mp 113°C. The product was shown to be identical with the authentic sample by comparison of IR spectra.

*Reaction of Ethoxycarbonyl-t-butylcarbodiimide with* N-*Benzoylglycine.* A solution of IIIg (85 mg, 0.5 mmol) and *N*-benzoyl glycine (89 mg, 0.5 mmol) in THF (8 m*l*) was refluxed for 3 hr. After the solution was kept standing overnight at room temperature, the solvent was removed under reduced pressure. The residue was applied to silica gel plates developed in 1,2-dichloroethane–ether (5 : 1). *N*-Benzoylglycine(*N'*-ethoxycarbonyl)amide was thus isolated in a 73% (91 mg) yield, mp 152—154°C. Recrystallization from ethanol gave an analytical sample which gave satisfactory analytical and IR data.