stirring. The reaction mixture was allowed to stand for 15 min and then 1.0-ml samples of the organic layer were withdrawn for qualitative and quantitative gc analysis. The products were isolated by preparative gc and characterized by their gc retention ratios and infrared and pmr spectra. Comparisons of these properties for the products were made with those of synthetic materials. In intermolecular competition reactions, N,N-dimethylaniline, *n*-butyllithium, and l-iodobutane were common reagents.

Intermolecular Competition Reactions. A. Triethylenediamine.—N,N-Dimethylaniline (6.1 ml, 50 mmol) was mixed with 5.7 g (50 mmol) of triethylenediamine and the mixture was treated with 13 ml of 1.6 *N* (20 mmol) *n*-butyllithium. 1-Iodobutane (2.3 ml, 20 mmol) was added slowly to control the vigorous reaction which was accompanied by the immediate formation of a precipitate. The reaction was continued for 2 hr as described above and quenched with ice, and the organic phase was analyzed by gc at 100 and 185°; see Table III.

B. Triethylamine.—N,N-Dimethylaniline (6.1 ml, 50 mmol) was mixed with 7.0 ml (50 mmol) of dry triethylamine. *n*-Butyllithium (13 ml, 20 mmol) was added to the cooled mixture with stirring. 1-Iodobutane (2.3 ml, 20 mmol) was added slowly over a period of 5 min since the reaction was very vigorous on rapid addition. On slow addition, the reaction proceeded controllably and was completed as described in the general procedure. The organic products reported in Table III were determined by gc analysis at 100° using aniline as a standard and at 185° with a benzhydryldimethylamine reference.

C. N,N-Diethylaniline.—N,N-Dimethylaniline (6.1 ml, 50 mmol) was mixed with 8.0 ml (50 mmol) of anhydrous monofree N,N-diethylaniline and 13 ml (20 mmol) of *n*-butyllithium. 1-Iodobutane (2.3 ml, 20 mmol) was added rapidly and the reaction was carried out as in the general procedure. After 2 hr, the reaction was quenched and the organic phase was analyzed by quantitative gc at 185° using benzhydryldimethylamine as the internal standard. Two product peaks were observed, Table III.

D. N-Methyl-N-ethylaniline.—N,N-Dimethylaniline (6.1 ml, 50 mmol) was mixed with 7.3 ml (50 mmol) of purified anhydrous N-methyl-N-ethylaniline and 13 ml (20 mmol) of *n*-butyllithium. After stirring briefly, 2.3 ml (20 mmol) of 1-iodobutane was added. When the reaction mixture was worked up as described in the general procedure, two product peaks (Table III) were observed in the gc of the organic phase at 185° with retention ratios of 0.525 and 0.618 using benzhydryldimethylamine as a standard.

E. N-Methyldiphenylamine.—N,N-Dimethylaniline (6.1 ml, 50 mmol) was mixed with 9.0 ml (50 mmol) of N-methyldiphenylamine and 13 ml (20 mmol) of *n*-butyllithium. 1-Iodobutane (2.3 ml, 20 mmol) was added rapidly and the reaction was carried out following the general procedure. The reaction was quenched after 2 hr, and the organic phase was analyzed by gc at 185°. The two product peaks observed (Table III) were determined using *o*-(diethylamino)biphenyl as an internal standard.

Intramolecular Competition Reactions. A.—N-Methyl-N-ethylaniline (14.7 ml, 0.1 mol) was mixed with 13 ml of 1.6 *N* (20 mmol) *n*-butyllithium at −10°. 1-Iodobutane (2.3 ml, 20 mmol) was added rapidly and the reaction was carried out according to the general procedure. The reaction was quenched after 2 hr and the organic phase when examined by gc at 185° showed only one product peak with a retention ratio of 0.618 *vs.* benzhydryldimethylamine as an internal standard. This peak corresponded to a 19.0% yield of $C_{13}H_{21}N$ products. Preparative gc was used to collect this material for infrared and pmr analysis. The infrared spectrum corresponded to that of N-ethyl-N-(1-pentyl)aniline except for very weak bands at 7.58 and 8.83 μ which are characteristic of two medium-intensity bands in N-methyl-N-(2-hexyl)aniline. In the pmr spectrum, δ values of the NCH_3 singlet at 2.59 ppm and NCHRR′ multiplet centered at 3.78 ppm in N-methyl-N-(2-hexyl)aniline were adequately separated from the NCH_2R overlapping quartet ($J = 6.9 \pm 0.1$ cps) of ethyl and multiplet of *n*-pentyl (centered respectively at 3.28 and 3.18 ppm) in N-ethyl-N-(1-pentyl)aniline to allow quantitative determination of the two isomeric products. The absence of a NCH_3 singlet at 2.78 ppm showed the separated product to be free of starting N-methyl-N-ethylaniline. The ratios of products as determined from pmr integral ratios was 3.3:1.0 methyl to ethyl position reaction for yields of 14.6% N-ethyl-N-(1-pentyl)aniline and 4.4% N-methyl-N-(2-hexyl)-aniline.

B. N-Methyl-N-(2-butyl)aniline.—N-Methyl-N-(2-butyl)-aniline (12.2 ml, 75 mmol) combined with 10 ml of 1.6 *N* (15 mmol) *n*-butyllithium and 1.6 ml (14 mmol) of 1-iodobutane was rapidly added to the mixture at −10°. The reaction was carried out as before and quenched after 2 hr, and the organic phase was examined using N-ethyl-N-(2-hexyl)aniline as a gc standard at 185°. Only one product peak was observed with a retention ratio of 1.37 relative to this standard. The infrared spectrum of a preparative gc sample was comparable with that of N-(2-butyl)-N-(1-pentyl)aniline but the pmr spectrum had a very weak singlet at 2.65 ppm. The integral ratio of this singlet and the $NCHR_2$ multiplet centered at 3.71 ppm was used for quantitative analysis indicating a maximum of 1.2% N-methyl-N-(3-methyl-3-heptyl)aniline in the over-all yield of 23.4%. The bulk of the product, at least 22.2%, was N-(2-butyl)-N-(1-pentyl)aniline.

Synthesis and Reactions of N-*p*-Tolylsulfonyl-N′-cyclohexylcarbodiimide

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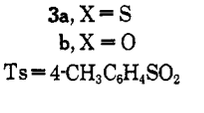
Received May 21, 1968

The synthesis of the title compound (**2a**) is described, and its reactions with several nucleophiles are described. Amino acid esters underwent addition–cyclization with **2a** giving imidazolidones, while cyclohexylamine and sodium azide afforded a guanidine and tetrazole, respectively. The condensation of N-carbobenzyloxyglycine with **2a** required a high temperature and gave only pyrolysis products.

Carbodiimides (**1**) are of considerable interest because of their use as agents in peptide synthesis[1] and more recently as oxidizing agents in dimethyl sulfoxide solution.[2] Our interest in sulfonylcarbodiimides (**2**) derived from the expectation that this highly polar diimide might have interesting uses in peptide chemistry. Ulrich[3] and coworkers have reported most completely on the synthesis of sulfonylcarbodiimides and some of their reactions. Using the Ulrich thiourea phosgenation procedure we have synthesized N-*p*-toluenesulfonyl-N′-cyclohexylcarbodiimide (TsCC) (**2a**) from the corresponding thiourea (**3a**) in 65% yield.

$$\underset{\mathbf{1}}{RN{=}C{=}NR'} \qquad \underset{\mathbf{2a}}{RSO_2N{=}C{=}NR'}$$

R = 4-$CH_3C_6H_4$; R′ = cyclohexyl



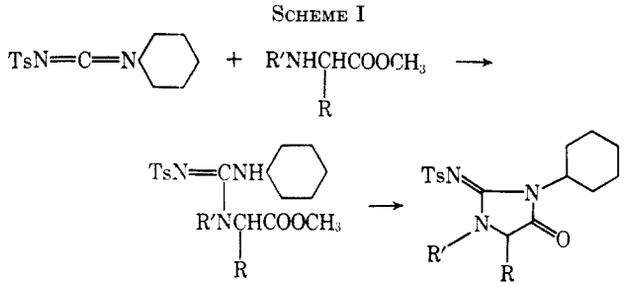
3a, X = S
b, X = O
Ts = 4-$CH_3C_6H_4SO_2$

(1) F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, **67**, 107 (1967).
(2) K. E. Pfitzner and J. G. Moffat, *J. Amer. Chem. Soc.*, **85**, 3027 (1963); **87**, 5661, 5670 (1965).
(3) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

TsCC is a white crystalline solid and is quite stable at 5° under anhydrous conditions over a period of at least 3–4 months. The urea (**3a**) was most conveniently prepared from *p*-toluenesulfonamide and cyclohexyl isothiocyanate. Alternatively, *p*-toluenesulfonyl isothiocyanate could be prepared by the method of Hartke[4] followed by treatment with cyclohexylamine to form **3a**, but the procedure was more lengthy. Even less rewarding was the attempt to convert the urea **3b** into **3a** with phosphorus pentasulfide.

When TsCC was allowed to react with molar equivalents of N-carbobenzyloxyglycine and L-phenylalanine methyl ester, the product corresponded to the combination of only the amino ester with TsCC. The same compound was obtained in the absence of the glycine derivative. It has been assigned the imidazolidone structure **5a** (Scheme I) on the basis of spectral data

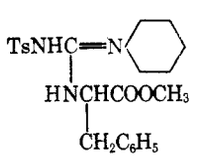
SCHEME I



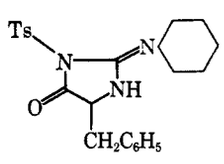
4a, R = $C_6H_5CH_2$; R′ = H
b, R = R′ = H
c, R = H; R′ = CH_3

5a, R = $C_6H_5CH_2$; R′ = H
b, R = R′ = H
c, R = H; R′ = CH_3

and elemental analysis and by analogy to a report[5] which showed that glycine *p*-nitrophenyl ester hydrobromide slowly reacted with dicyclohexylcarbodiimide to give an imidazolidone. When this reaction mixture was worked up immediately after the TsCC had been consumed, a gummy product showing two NH absorptions and a carbonyl peak at 30-cm^{-1} higher frequency than that in **5a** was isolated. This material also showed an nmr peak at δ 3.59 ppm corresponding to a methyl ester and was undoubtedly the intermediate **4a** in which cyclization had not yet occurred. When **4a** was heated in methanol solution, **5a** was formed in excellent yield. It was interesting to note that **4a** showed $[\alpha]^{27}D$ + 49.3°, but that the cyclic product **5a** was completely racemic whether formed at room temperature or above. Enolization of the carbonyl function in **5a** must therefore be occurring. Since the infrared carbonyl absorption was of the expected intensity, a ferric chloride test for enol content was negative and **5a** was insoluble in dilute alkali; the enolization equilibrium was apparently established very rapidly but strongly favored the carbonyl form. Alternative structures **6** and **7** can be visualized for the



6

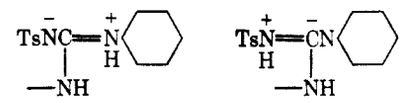


7

(4) K. Hartke, *Arch. Pharm.*, **299**, 174 (1966).

(5) D. F. TeTar, R. Silverstein, and F. F. Rogers, *J. Amer. Chem. Soc.*, **88**, 1024 (1966).

intermediate ester and imidazolidone, respectively. The spectral data are also consistent with these structures, but we feel that **4a** and **5a** are to be preferred. Certainly **4a** can be considered thermodynamically more stable than **6** since the resonance form **8** which contributes to **4a** should be considerably more stable than the corresponding **9**, which has a positive charge

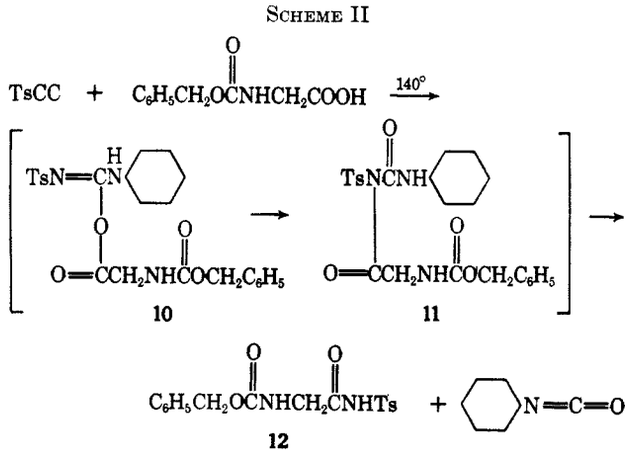


8 **9**

close to the electronegative tosyl group.[6] The same argument holds for the stability relationship between **5a** and **7**. If we accept the intermediacy of the ester **4a**, it seems extremely unlikely that the ring closure to imidazolidone might occur at the nitrogen atom having the *lower* nucleophilicity, giving **7**. For these reasons, we assign the structure **5a** to the imidazolidone.[7] When glycine and sarcosine are allowed to react with TsCC, imidazolidones **5b** and **5c** were formed. The N-methyl compound **5c** showed an intense azomethine absorption within 8 cm^{-1} of this same absorption peak in **5a**. Since **5c** *must* have an *exo*-azomethine grouping, this similarity between **5a** and **5c** supports the *exo*-azomethine structure for **5a**.

In a further attempt to make use of TsCC in amino acid couplings, we examined the conditions necessary to cause it to react with N-carbobenzyloxyglycine. No reaction occurred in methylene chloride, and the higher boiling solvents dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) could not be used because TsCC was slowly consumed by them even in the absence of N-carbobenzyloxyglycine. When the two reactants were fused at *ca.* 140°, an almost quantitative yield of N-(N-carbobenzyloxyglycyl)-*p*-toluenesulfonamide (**12**) was obtained. Cyclohexylisocyanate was formed simultaneously and isolated as N,N′-dicyclohexylurea after reaction with cyclohexylamine. To explain these results we propose that the expected intermediate **10** formed and rearranged rapidly[1] to the acylurea **11**. The pyrolysis of **11** (Scheme II) at 140°

SCHEME II



10 **11**

12

(6) In ref 3, Ulrich and coworkers established the position of the N–H proton in a similar system by chemical shift analogy with N-sulfonyl-N′-alkylureas. In **4a**, strong absorption by the aromatic protons in the δ 7.22–7.82-ppm region overlaps the absorption of NH protons and thus makes the detection of N–H absorption difficult. Lack of absorption of >8.5 ppm in **4a** makes probable the absence of an N–H proton adjacent to the tosyl group.

(7) For a discussion of a sulfonylamidine structural investigation, see S. J. Angyal and W. K. Warburton, *Aust. J. Sci. Res.*, **4A**, 93 (1951).

might then afford the observed products.[8] It would be most interesting if the O-acylurea **10** could be isolated, but attempts to carry out the reaction at lower temperatures or in the presence of catalysts failed.

In 1963, Aumueller[9] suggested that TsCC might be intermediate in the formation of N,N′-bis-*p*-tolyl-N″-cyclohexylguanidine when cyclohexyl isocyanide reacted with Chloramine-T in aqueous acetone solution. We have found that TsCC is very rapidly hydrated in this medium[10] giving the urea **3b**. TsCC was also converted very readily into the guanidine **13** and tetrazole **14** by reaction with cyclohexylamine and sodium azide, respectively. Both of these compounds showed the characteristic strong absorption (*ca.* 1610 cm^{-1}) for the tosylimino group. The ease with which these derivatives were formed is consistent with the electrophilic character of the central carbon atom of TsCC.

It occurred to us that this enhanced electrophilicity might cause TsCC to have some utility as an oxidizing agent in DMSO solution since dicyclohexylcarbodiimide (DCC) has been used in this medium. The proposed mechanism[2] of this reaction requires an intermediate formed by addition of the nucleophilic oxygen atom of DMSO to the central electrophilic carbon of DCC. Thus we might expect TsCC to form such an intermediate quite readily because of its enhanced electrophilicity. We examined the oxidation of benzhydrol to benzophenone and found that oxidation proceeded readily both in the presence and absence of acid catalysis. Yields, however, were not high even in the presence of excess TsCC. As previously mentioned, we have observed that both DMSO and DMF destroy TsCC rapidly at room temperature. These rapid side reactions may explain the low oxidation yields.

Experimental Section

All melting points were determined on a Nalge hot stage and are uncorrected. Infrared spectra were obtained with Perkin-Elmer grating spectrophotometers, Models 237B or 257, in KBr or NaCl cells. Nmr spectra were obtained on a Varian Associates Model A-60 or HA-100 spectrometer using tetramethylsilane as internal standard. Tlc analyses were carried out on Eastman precoated silica gel sheets, Type 6060, with fluorescent indicator. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

N-*p*-Toluenesulfonyl-N′-cyclohexylthiourea (3a).—To a solution of 8.56 g (0.05 mol) of *p*-toluenesulfonamide in 35 ml of aqueous sodium hydroxide containing 2.0 g (0.05 mol) of NaOH was added a solution of 7.06 g (0.05 mol) of cyclohexyl isothiocyanate in 20 ml of acetone. The mixture was stirred magnetically and refluxed in an oil bath maintained at 63 ± 2° for 15 hr. A small amount of insoluble material was filtered; the filtrate was concentrated to *ca.* 10 ml *in vacuo* and acidified with concentrated HCl. The precipitated thiourea was filtered, washed with a little cold water, and recrystallized from 75% aqueous EtOH to give 9.5 g (61%), mp 173–175°, of pure product in two crops: ir (Nujol) 3318 (NH), 1375, 1160 cm^{-1} (SO_2); nmr ($CDCl_3$), δ 8:11 (d, 1, J = 8 Hz, NHC_6H_{11}), 7.87–7.29 (q, J_{AB} = 8 Hz, *p*-tolyl), 4.06 (s, broad, 1, –CH–NH–), 1.95–1.01 (m, 10, cyclohexyl).

N-*p*-Toluenesulfonyl-N′-cyclohexylcarbodiimide (TsCC) (2a).—To a stirred suspension of 8.3 g (26.6 mmol) of N-*p*-toluenesulfonyl-N′-cyclohexylthiourea in 30 ml of dry chlorobenzene was added a solution of 3.0 g (30 mmol) of phosgene in 20 ml of dry chlorobenzene during 30 min at 3–5° and the mixtue was stirred at room temperature for 3 hr. A tlc (C_6H_6–$CHCl_3$, 1:1) plate indicated the complete absence of thiourea in the reaction mixture. It was refluxed for 2 hr during which time a slow stream of dry nitrogen was bubbled through the clear solution to expel unreacted phosgene. The chlorobenzene was removed *in vacuo* to give a viscous oil to which 25 ml of pentane was added. The solution was evaporated at room temperature to give 7.3 g (100%) of slightly impure TsCC. Crystallization from a mixture of 250 ml of pentane and 20 ml of benzene at 0–5° yielded 6.2 g (83%), mp 55–56°, of a white powder which was recrystallized from pentane to give 4.75 g (65%) of pure TsCC: mp 56–57°; ir ($CHCl_3$) 2180 (N=C=N), 1332, 1160 cm^{-1} (SO_2); nmr ($CDCl_3$), δ 7.88–7.00 (q, 4, J_{AB} = 8 Hz, *p*-tolyl), 3.70 (s, 1), 2.40 (s, 3, Ar–CH_3), 1.96–1.00 (m, 10 H).

Anal. Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.42; H, 6.52; N, 10.07; S, 11.50. Found: C, 60.78; H, 6.75; N, 9.74; S, 11.38.

1-Cyclohexyl-2-*p*-toluenesulfonimido-4-benzyl-5-imidazolidone (5a). In the Presence of Carbobenzyloxyglycine.—To a stirred solution of 617 mg (3.44 mmol) of freshly prepared L-phenylalanine methyl ester and 720 mg (3.44 mmol) of carbobenzyloxyglycine in 15 ml of methylene chloride was added 1.07 g (3.84 mmole) of TsCC in one lot, and the solution was stirred 3 hr at room temperature. A tlc plate (C_6H_6–$CHCl_3$, 3:7) indicated the complete absence of TsCC in the reaction mixture. Evaporation of the solvent *in vacuo* yielded 2.06 g of a gum which was dissolved in 50 ml of ethyl acetate, and the solution was washed with 1 *N* NaOH (two 10-ml portions) and water (two 10-ml portions) and dried. Removal of solvent furnished 1.36 g of a sticky mass which on crystallization from aqueous methanol yielded 961 mg (66%) of **5a** as colorless cubes, mp 185–189°. Two recrystallizations from methanol furnished an analytical sample: mp 193–194.5°; ir ($CHCl_3$) 3372 (NH), 1700 (C=O), 1612 cm^{-1} (SO_2N=C); nmr ($CDCl_3$), δ 8.17 (s, 1, NH), 7.90–7.32 (q, 4, J_{AB} = 8 Hz, *p*-tolyl), 7.24 (s, 5, $C_6H_5CH_2$), 4.37 (t, 1, J = 5 Hz, O=C—CH–), 3.16 (d, 2, J = 5 Hz, –CH—CH_2-C_6H_5), 2.47 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{23}H_{27}N_3O_3S$: C, 64.93; H, 6.40; N, 9.88; S, 7.52. Found: C, 64.90; H, 6.42; N, 10.05; S, 7.51.

Isolation of Intermediate 4a.—A freshly prepared solution of 303.6 mg (1.7 mmol) of L-phenylalanine methyl ester, $[\alpha]^{27}D$ +13.7 (*c* 5, $CHCl_3$), in 6 ml of chloroform was added to 474 mg (1.7 mmol) of TsCC, and its rotation was observed at various intervals. After 5 min the observed rotation was +6.40° and did not change on standing for 720 min. On the assumption that the reaction was complete, $[\alpha]^{27}D$ +49.3° was calculated. Removal of solvent *in vacuo* at room temperature yielded a gum: ir ($CHCl_3$) 3420, 3320 (NH), 1735 (ester C=O), 1595 cm^{-1} (SO_2 N=C); nmr ($CDCl_3$), δ 3.59 (s, 3, $COOCH_3$). The gum was dissolved in 12 ml of methanol and gently refluxed for 12 hr. Removal of solvent furnished a white solid which was twice crystallized from methanol to give white cubes, mp 192–194°, identified as **5a** by ir, tlc, and mixture melting point.

1-Cyclohexyl-2-*p*-toluenesulfonimido-5-imidazolidone (5b).—TsCC (1.12 g, 4 mmol) was allowed to react with 4 mmol of glycine methyl ester prepared from 502 mg of the hydrochloride using 0.8 ml of triethylamine in 15 ml of methylene chloride. The product was obtained by the procedure outlined for **5a**: yield, 1.20 g (90%); mp 203–205° after crystallization from methanol. Recrystallization from aqueous methanol furnished an analytical sample of **5b** as colorless needles: mp 205–206°; ir ($CHCl_3$) 3360 (NH), 1755 (C=O), 1615 cm^{-1} (SO_2N=C); nmr ($CDCl_3$), δ 7.91–7.23 (m, 5, *p*-tolyl and NH), 4.08 (d, J = 1 Hz, O=C—CH_2—NH), 2.41 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{16}H_{21}N_3O_3S$: C, 57.30; H, 6.31; N, 12.53; S, 9.54. Found: C, 57.33; H, 6.55; N, 12.51; S, 9.60.

1-Cyclohexyl-2-*p*-toluenesulfonimido-3-methyl-5-imidazolidone (5c).—To a suspension of 580 mg (4.15 mmol) of sarcosine methyl ester hydrochloride in 15 ml of dry methylene chloride was added 0.64 ml of triethylamine. The mixture was stirred for 30 min at room temperature, and to this clear solution 1.20 g (4.30 mmol) of TsCC was added. After stirring for 20 min the solvent was removed *in vacuo*, and the residue was worked up as described in the above experiment to yield 1.59 g of a gum. It was dissolved in 20 ml of methanol, and the solution was refluxed for 18 hr. The methanol was evaporated to a volume of *ca.* 8 ml and then allowed to cool. The crystalline product was filtered, washed with a little methanol, and dried (weight,

(8) F. Zetzsche, H. E. Meyer, H. Overback, and H. Lindlar [*Chem. Ber.*, **71**, 1512, 1516 (1963)] reported that 2-benzamidopyridine was formed when N,N′-bis(2-pyridyl)carbodiimide and benzoic acid were fused at *ca.* 200°. This result parallels that just discussed.

(9) R. Aumueller, *Angew. Chem. Intern. Ed. Engl.*, **2**, 616 (1963).

(10) It has been reported that TsCC also hydrates readily in dioxane–water mixtures; *cf. Chem. Abstr.*, **64**, 19506*a* (1966).

1.14 g). From the mother liquors another 0.07 g of the compound was obtained: total yield, 1.21 g (74%); mp 179–181°. Recrystallization from methanol provided an analytical sample as colorless needles: mp 180–181°; ir ($CHCl_3$) 1754 (C=O), 1620 cm^{-1} (SO_2N=C); nmr ($CDCl_3$) δ 7.93–7.22 (q, 4, J_{AB} = 8 Hz, *p*-tolyl), 4.00 (s, 3, NCH_3), 2.42 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{17}H_{23}N_3O_3S$: C, 58.44; H, 6.64; N, 12.03; S, 9.16. Found: C, 58.61; H, 6.92; N, 11.96; S, 9.30.

N-(N-Carbobenzyloxyglycyl)-*p*-toluenesulfonamide (12).—A mixture of 418 mg (2 mmol) of carbobenzyloxyglycine and 556 mg (2 mmol) of TsCC was stirred for 90 min at 140 ± 2° under anhydrous conditions. The melt was allowed to attain room temperature; the solid cake was broken up and extracted with 20 ml of refluxing hexane for 15 min. After cooling, the precipitated product was filtered, washed with a little hexane, and dried to give 740 mg of a powder, mp 134–136°. It was dissolved in 25 ml of benzene treated with a pinch of charcoal and filtered. The filtrate was concentrated to *ca.* 10 ml and diluted with an excess of hexane. The precipitate was filtered and recrystallized from benzene–hexane giving 527 mg (73%) of pure **12** as a white solid: mp 139–140°; ir ($CHCl_3$) 3420 (NH), 1720–1700 (C=O); nmr (DMSO-d_6), δ 7.94–7.36 (q, 4, J_{AB} = 8 Hz, *p*-tolyl), 7.35 (s, 5, $C_6H_5CH_2O$), 5.05 (s, 2, C_6H_5–CH_2–O–), 3.74 (d, 2, J = 6 Hz, –CH_2–NH–), 2.40 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{17}H_{18}N_2O_5S$: C, 56.35; H, 5.01; N, 7.73; S, 8.83. Found: C, 56.19; H, 4.96; N, 7.80; S, 8.76.

To the hexane extracts of the reaction mixture, cyclohexylamine was added. Within a short time a white precipitate formed and was filtered, washed with little hexane, and dried to give 340 mg (76%) of a white solid, mp 234–235°. This was identified as N,N'-dicyclohexylurea by mixture melting point and ir spectrum.

Reaction of TsCC with Aqueous Acetone.—A solution of 53 mg (0.19 mmol) of TsCC in 1 ml of acetone and 0.15 ml of water was stirred at room temperature. After stirring for 2 hr the tlc (C_6H_5–$CHCl_3$; 3:7) spot corresponding to TsCC had disappeared; however, stirring was continued for another 6 hr. Upon addition of 5 ml of water, a white precipitate was formed and filtered, yield 52 mg (93%). Recrystallization from aqueous acetone gave white needles, mp 175–177°, identified as **3a** by tlc and mixture melting point.

N,N'-Dicyclohexyl-N''-*p*-toluenesulfonylguanidine (13).—To a stirred solution of 99 mg (1 mmol) of cyclohexylamine in 5 ml of methylene chloride was added 278 mg (1 mmol) of TsCC. After the mixture was stirred for 1 hr at room temperature, a tlc plate (C_6H_6–$CHCl_3$; 1:1) indicated the complete absence of TsCC. Evaporation of solvent *in vacuo* furnished 376 mg (100%) of a white amorphous solid, mp 160–165°, which was crystallized from benzene–hexane to give 345 mg (94%) of the guanidine **13**, mp 164–166°. Recrystallization from benezne–hexane yielded an analytical sample of **13** as fine needles: mp 165–166°; ir ($CHCl_3$) 3444 and 3320 (NH), 1590 cm^{-1} (SO_2N=C).

Anal. Calcd for $C_{20}H_{31}N_3O_2S$: C, 63.64; H, 8.28; N, 11.13; S, 8.47. Found: C, 63.66; H, 8.10; N, 11.47; S, 8.77.

1-Cyclohexyl-5-*p*-toluenesulfonimido-2(4)-H-tetrazole (14).—A mixture of 834 mg of TsCC, 195 mg (3 mmol) of sodium azide, and 20 ml of dimethoxyethane was stirred for 12 hr at room temperature. To this suspension 1 ml of water was added, and stirring was continued for another 2 hr. Evaporation of the solvent *in vacuo* gave a white solid which was dissolved in 15 ml of 1 *N* sodium hydroxide. The solution was filtered, the filtrate was acidified with concentrated HCl, and the precipitate was filtered, washed with cold water, and dried to give 920 mg (96%) of crude tetrazole **14**. Two recrystallizations from chloroform furnished an analytical sample: mp 232–233°; ir (Nujol) 3120 (NH), 1628 cm^{-1} (SO_2N=C).

Anal. Calcd for $C_{14}H_{19}N_5O_2S$: C, 52.33; H, 5.94; N, 21.79; S, 9.96. Found: C, 52.28; H, 5.94; N, 22.07; S, 10.24.

Oxidation of Benzhydrol Using TsCC. A. Pyridinium Trifluoroacetate[2] As Catalyst.—A reaction medium was prepared by adding 3 ml of DMSO to a mixture of 0.16 ml of dry pyridine and 0.08 ml of trifluoroacetic acid in 3 ml of benzene. To 184 mg (1 mmol) of benzhydrol, 3 ml of this mixture was added followed by 556 mg (2 mmol) of TsCC. The mixture was stirred for 36 hr at room temperature in a stoppered flask. Tlc analysis (C_6H_6–$CHCl_3$, 1:1) of the reaction mixture indicated that after 8 hr there was no further progress of the oxidation. The reaction mixture was diluted with 30 ml of ether and washed successively with water (three 10-ml portions), 1 *N* NaOH (two 10-ml portions), and water (one 10-ml portion) and dried. Removal of solvent *in vacuo* furnished 139 mg of an oil which showed at least four spots on a tlc plate. Two of these spots had the same R_f as benzhydrol and benzophenone. The total mixture was dissolved in 5 ml of benzene–hexane (1:1) mixture, treated with decolorizing carbon, and filtered, and the filtrate was evaporated *in vacuo* to yield 70 mg of an oil. This was dissolved in 1 ml of ethanol and treated with a slight excess of ethanolic 2,4-dinitrophenylhydrazine containing HCl. After 2 hr at room temperature, the orange 2,4-dinitrophenylhydrazone (DNP) was filtered, washed, and dried: yield, 39 mg; mp 242–244°. There was no depression in melting point when on admixture the authentic 2,4-DNP of benzophenone.

B. Without Catalyst.—To a stirred solution of 834 mg (3 mmol) of TsCC in 5 ml of DMSO was added 552 mg (3 mmol) of benzhydrol. The stirring was continued for 22 hr at room temperature; however, tlc analysis indicated that no further oxidation occurred after 4 hr. The mixture was diluted with 50 ml of ether and worked up as described in part A to give 668 mg of an oil containing a small amount of solid. Upon acidification the sodium hydroxide washing gave 346 mg (39%) of the urea **3a**. The oily product was found by tlc to be a mixture of at least four compounds. It was chromatographed on an alumina column (6.6 g, Woelm "neutral" alumina, activity I), and the column was developed by successive elution with hexane and ether. The first hexane eluate (260 ml) was evaporated *in vacuo* to give 345 mg of an oil. A tlc (C_6H_6 solvent) of this oil indicated the presence of two close spots, the major one corresponding to benzophenone. The oil was dissolved in 15 ml of ether, washed with water (two 5-ml portions), and dried, and the solvent was removed to give 290 mg of a liquid: ir (liq film) 1655 cm^{-1} (C=O). It was converted into its 2,4-DNP giving 250 mg (23%) of impure 2,4-DNP which on crystallization from acetic acid furnished 150 mg (14%) of pure 2,4-DNP, mp 243–244°, identified as in part A.

Registry No.—**2a,** 5287-13-8; **3a,** 5530-82-5; **4a,** 17703-97-8; **5a,** 17719-27-6; **5b,** 17703-94-5; **5c,** 17703-95-6; **12,** 17719-28-7; **13,** 908-18-9; **14,** 17703-98-9.

Acknowledgment.—We are grateful to the National Institutes of Health, Grant No. 501 AM11070, for financial support of this research.