bined chloroform extracts to dryness under reduced pressure, the residue was crystallized from petroleum ether (60–70°). A yield of 0.81 g. (54%) of material melting at 198–200° was obtained. Recrystallization from benzene–petroleum ether (60–90°) raised the melting point to 201–202° identical with that of erythralosamine in the same apparatus. A mixture melting point gave no depression, and the X-ray diffraction patterns were identical.

(b) **Isolation of Neutral Glycoside.**—The aqueous solution from the above experiment was evaporated to dryness under reduced pressure at room temperature. The residue was extracted with four 15-ml. portions of boiling benzene filtering each extract. Evaporation of the combined extracts under reduced pressure left a residue of 0.14 g. This was distilled at a bath temperature of 90–120° under a pressure of 0.05 mm. The infrared spectrum had strong absorption at 2.87 and 2.95 μ and weak absorption in the carbonyl region at 5.9 μ. This spectrum differed from that of methyl mycaroside.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.54; H, 9.12; CH_3O (1), 17.6. Found: C, 52.54; H, 9.07; CH_3O, 13.6.

Reduction and Methanolysis of Erythromycin C.—A solution of 1 g. of erythromycin C in 6 ml. of methanol was reduced with sodium borohydride and subsequently subjected to acid methanolysis as described for the preparation of X-O-desosaminyldihydroerythronolide.[8] The reduction product (215 mg.) obtained melted at 205–207°. The infrared spectrum and the X-ray diffraction pattern were indistinguishable from those of 5-O-desosaminyldihydroerythronolide[4] prepared from erythromycin.

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(8) M. V. Sigal, Jr., P. F. Wiley, K. Gerzon, E. H. Flynn, U. C. Quarck and O. Weaver, THIS JOURNAL, **78**, 388 (1956).

INDIANAPOLIS, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Polynitrogen Systems from the Hydrazinocarbonic Acids. V.[1] Aminolytic Reactions of N,N-Diphenylcarbamyl Azide[2]

BY F. L. SCOTT[3a] AND M. T. SCOTT[3b]

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The possible competition between Curtius rearrangement of diphenylcarbamyl azide (Ic) and displacement of its azide function by extraneous bases has been examined. In pyridine or ethanol as solvent the Curtius reaction was dominant, the sole products of aminolysis being 1,1-diphenyl-4-substituted semicarbazides (IV). When various amines were employed as both solvents and reactants, effective competition with the facile intramolecular rearrangement was realized. With amines of b.p. <110° and pK_a's of from 9.7 to 11.2, displacement of the azide moiety of Ic was the sole process encountered yielding ureas of type V. Those bases with b.p.'s from 110–185° and pK_a's from 4 to 9 either resulted in a mixture of azide displacement and Curtius reaction or else in the latter alone. Those bases with b.p.'s >185° (and pK_a's of *ca.* 9–10) formed symmetrically substituted ureas such as VI. The trends operative within the various classes of reaction with pK_a and temperature variations have been explored.

In another paper[1] of this series we formulated the Curtius rearrangement of certain carbamyl azides, *e.g.*, Ia, as involving cyclic transition states of type II (*cf.* ref. 2). We then related the inability to rearrange of some of the substituted carbamyl azides, *e.g.*, Ib, to the incapability of the specific amino groups therein for adequate sustenance of the electronic requirements, *viz.*, 'onium character, that such rearrangement would necessitate. With the very low driving force toward Curtius change that an azide such as Ib then possesses, alternative reactions compete effectually with its possible rearrangement. Such competing reactions may include simple azide displacements[4] (mode B, Fig. 1) or tetrazole closures[5] or perhaps homolytic scissions[6] of the azide function. In general such processes are potentially competitive even with the facile Curtius rearrangements of azides such as Ia, but under the conditions so far investigated the driving forces of this latter class of carbamyl azide toward rearrangement have been sufficiently large so as to inhibit the intrusion of any other mode of reaction upon the Curtius transformation.

The present work was an endeavor to intercept this facile rearrangement. An azide was accordingly chosen, namely, N,N-diphenylcarbamyl azide (Ic) which had been previously[7] observed to undergo the Curtius reaction readily and the extent to which the presence of extraneous bases interfered with the Curtius process was examined. In ethanolic solution, the reactions of Ic with various amines resulted in the exclusive formation of the corresponding 1,1-diphenyl-4-substituted semicarbazides (IV) and thus corresponded to dominance of the Curtius mode of reaction. The same result was observed when pyridine was used as the reaction medium, only therein, under our conditions, the velocity of rearrangement of Ic was roughly fifty times that of the corresponding reaction in refluxing ethanol.[8] When amines of very low nucleophilicity were employed, or when no additional bases were present, both solvents themselves induced Curtius transformations in Ic. While in ethanol the product obtained was 1,1-diphenyl-2-carbethoxyhydrazine[7a]; in pyridine both 1,1,5,5-tetraphenylcarbohydrazide (IVa) and another disproportionation product of formula $C_{19}H_{24}N_3O$ were isolated.

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(1) Part IV, this series, F. L. Scott, A. J. Kocjarski and J. Reilly, *J. Org. Chem.*, in preparation.

(2) A previous preliminary communication mentioning some of these results was F. L. Scott, *Chem. & Ind.*, 959 (1954).

(3) (a) To whom inquiries concerning reprints are to be sent, Pennsalt Chem. Corp., P.O. Box 4388, Phila. 18, Pa.; (b) Department of Chemistry, Marymount College, Los Angeles 24, California.

(4) Compare M. S. Newman, S. H. Lee, Jr., and A. B. Garrett, THIS JOURNAL, **69**, 113 (1947).

(5) Compare F. L. Scott, F. C. Britten and J. Reilly, *J. Org. Chem.*, **21**, 1519 (1956).

(6) A. Bertho, *J. prakt. Chem.*, **120**, 94 (1929).

(7) (a) R. Stolle, *Ber.*, **57**, 1065 (1924); (b) R. Stolle, N. Nieland and M. Merkle, *J. prakt. Chem.*, **116**, 192 (1927); (c) R. Stolle, N. Nieland and M. Merkle, *ibid.*, **117**, 185 (1927); (d) R. Stolle and M. Merkle, *ibid.*, **119**, 275 (1928).

(8) This difference is largely due to the temperature differential between the two reactions.

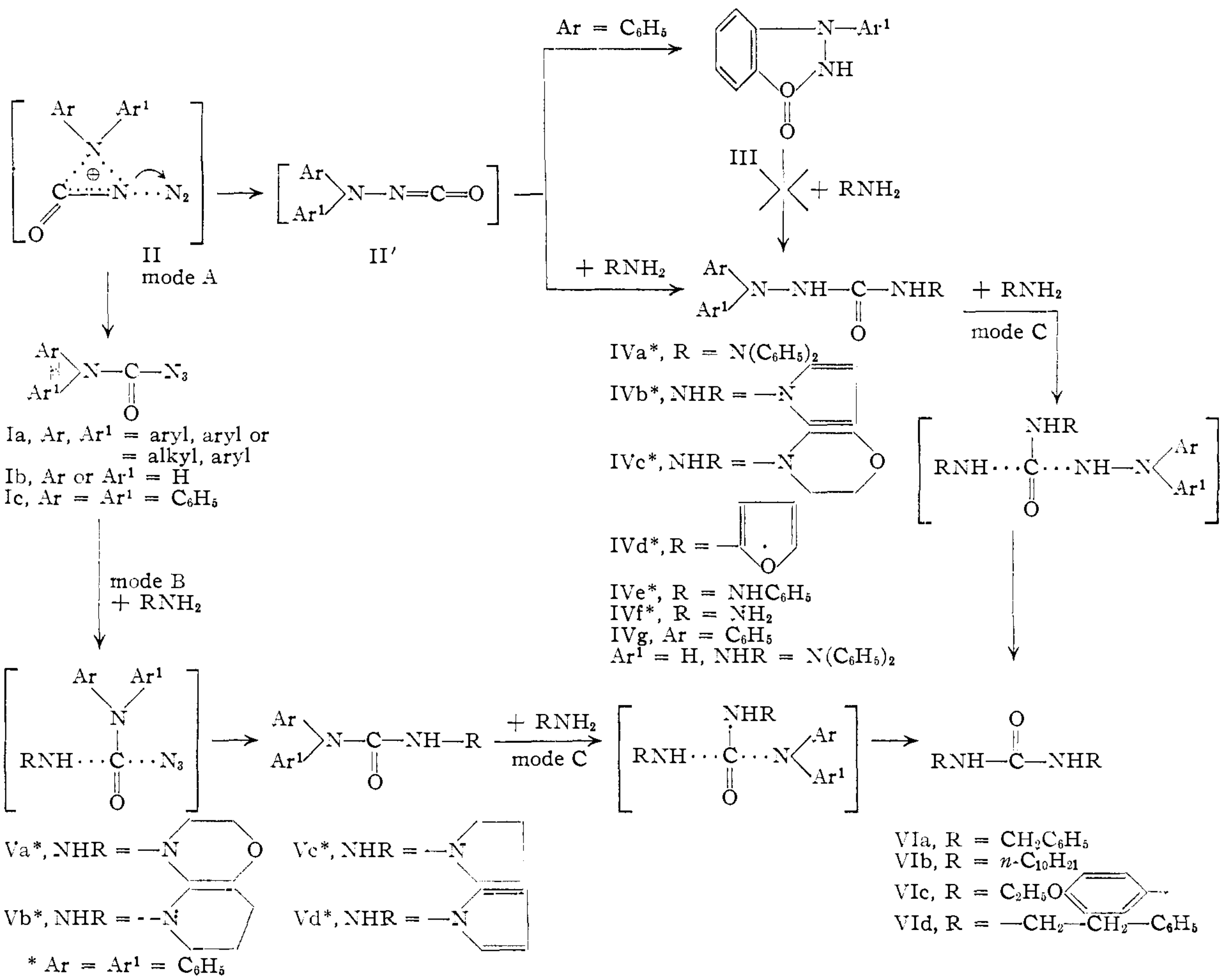

Fig. 1.

Under more forcing conditions, *viz.*, with the amines concerned employed as both solvents and reactants, the desired competition was realized and all subsequent discussion refers to reactions conducted thus and the phenomena detected therein. All the aminolyses were conducted at reflux temperatures for 1 hr. and with an amine to azide ratio of ten to one. Two variables appeared to be of prime importance in determining which course of reaction Ic adopted in a particular amine solvent, and these were the basicity, or pK_a,[9] and boiling point of the base. The former was an anticipated parameter[4] and the latter physical property is also clearly important because under the chosen conditions it corresponds to the reaction temperature.

The reactions of Ic conducted thus fell into 3 roughly divided classes. We found that amines (group a) with b.p.'s $<110°$ and pK_a values from 9.7 to 11.2 resulted solely in azide displacements of the type symbolized by mode B, Fig. 1, with the formation exclusively of ureas of type V.[10] Those bases used in the present work which possess those physical properties are as follows[11a,b]: allylamine (53°, 9.7, 60); *n*-amylamine (103°, 10.7, 81); piperidine (106°, 11.2, 92) and pyrrolidine (89°, 11.1, 86). Azide displacement reactions of mode B are therefore encountered with amines of high basicity and low b.p. While isopropylamine[11a] (34°, 10.6) also conforms to these specifications, it had previously[12] been found to exhibit some steric

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[9] No distinction was made in the present work between the basicity (toward proton) and the nucleophilicity (toward carbon) of the amine medium. Contrast, for example, C. G. Swain and C. B. Scott, This Journal, **75**, 141 (1953), and J. O. Edwards, *ibid.*, **76**, 1540 (1954), wherein such distinction is elaborated. The pK_a data cited herein were taken from standard compilations in the literature, where they were generally determined in aqueous media and at ambient temperature. The pK_a values quoted therefore do not represent accurately the "basicities" of our refluxing amine media. Irrespective of this, the behavior of Ic in basic environments does appear to parallel the "basicity" (pK_a) of such environment. Because of lack of information on the variations in both pK_a's and nucleophilicities with drastic medium and temperature changes, no further refinement of viewpoint on this topic can be offered at this time. A possibility also existed that the dielectric constants of the basic media might influence the balance between the modes of reaction. However, considering the values of the dielectric constants involved [as listed by A. A. Maryott and E. R. Smith, *Natl. Bur. Standards Circ.*, 514, August (1951)], no such influence appeared to be directly concerned. Compare the similar conclusions of Newman, *et al.*, ref. 4.

[10] Compounds V were also independently synthesized by the reaction of the appropriate amine and diphenylcarbamyl chloride in pyridine.

[11] In numerical order after each amine we append (a) its b.p. and pK_a. The other number occasionally cited with these data refers to either (b) the yield % of urea of type V the amine afforded or (c) the yield % of urea of type VI it gave.

[12] *Cf.* (a) E. McC. Arnett, J. G. Miller and A. R. Day, This Journal, **72**, 5635 (1950); (b) F. H. Wetzel, J. G. Miller and A. R. Day, *ibid.*, **75**, 1150 (1953); (c) H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953); (d) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

hindrance toward related acyl reactions.[12c,d] Its reactions with Ic also displayed the operation of steric influences. Thus when Ic was refluxed in a ninefold excess of this amine as sole solvent for 45 minutes, 82% Ic was recovered from the reaction liquor and a 6% yield of 1,1-diphenyl-4-isopropyl semicarbazide was formed. Accordingly, none of the sterically inhibited intermolecular (mode B) displacement was detected, instead a slow intramolecular rearrangement of Ic occurred followed by the amination of the isocyanate (II′) thus produced.

With those amines (group b) with b.p.'s from 110–185° and pK_a's from 4 to 9, the aminolyses of Ic effected resulted in either a mixture of azide displacement and Curtius rearrangement or else in the latter process alone. At the lower temperature levels of this group, it was evident (a) that keeping the basicity of the medium low, *i.e.*, its $pK_a < 5$ or 6 resulted in predominance of Curtius change with Ic, and (b) conversely, that at an approximately constant temperature, increasing the medium basicity resulted in sharply increased incursion of mode B reactions. These conclusions follow from the data obtained with pyrrole[11a] (131°, *ca.* 4.0), morpholine (126°, 8.7) and cyclohexylamine (134°, 10.6). The reactions of these amines with Ic corresponded respectively to the formation (1) of an 84% yield of the substituted semicarbazide IVb, (2) of a mixture of the semicarbazide IVc, 72% yield, and ureide Va, 4% yield, and (3) of a mixture of 1,1-diphenyl-4-cyclohexylsemicarbazide, 65% yield, and 1,1-diphenyl-3-cyclohexylurea, 35% yield. In this regard it is interesting to note that maintaining the basicity level high, an increase in temperature above the level (*ca.* 130°) just cited can again increase the relative amount of Curtius transformation as occurred, *e.g.*, with furfurylamine[11a] (145°, *ca.* 9.5 to 10) whose aminolysis of Ic afforded a 75% yield of the corresponding semicarbazide IVd. At the upper temperature levels of this group when the amine medium possesses a high basicity, a new reaction intrudes upon the observation of the Curtius change. This new process involves a dual displacement as indicated in mode C and leads to the formation of symmetrically substituted ureas of type VI. That a high basicity is necessary for its observance is suggested by the reactions of Ic in aniline[11a] (185°, 4.6) and benzylamine (185°, 9.3), which reactions afford respectively an 80% yield of 1,1,4-triphenylsemicarbazide and a mixture of 1,1-diphenyl-4-benzylsemicarbazide, in 25% yield, and 1,3-dibenzylurea (VIa) in 50% yield.

The third class of amines (group c) employed had b.p.'s between 185 and 250°, and pK_a's of from 9.3 to 10.0. The reactions of such bases with Ic resulted exclusively in the formation of ureides such as VI. The bases of this type which we used were β-phenylethylamine[11a,c] (198°, 9.8, 42), *n*-decylamine (221°, *ca.* 10.0, 90) and *p*-phenetidine (254°, 9.7, 71). While we have not formally included phenylhydrazine[11a] (244°, 5.2) in this class, its b.p. is such as to merit comparing its hydrazinolysis of Ic with the corresponding *p*-phenetidine reaction. The only product we were able to isolate from the reaction of phenylhydrazine with Ic was 1,1,5-triphenylcarbohydrazide (IVe) in 53% yield. It can thus be seen that a reduction in pK_a of 4.5 units in the basic environment again restores Curtius type reactions to dominance even over the mode C processes.

An effort was made to decide whether mode A and/or mode B processes were precursors to the mode C reactions. Benzylamine was chosen as the prototype base and in separate experiments it was refluxed for 1 hr. without further solvent, with the product of its mode B reaction with Ic, namely, 1,1-diphenyl-3-benzylurea and also with the derivative resulting from its mode A aminolysis of Ic, *viz.*, 1,1-diphenyl-4-benzylsemicarbazide. In the latter reaction *ca.* 60% of the substituted semicarbazide was recovered and 20% 1,3-dibenzylurea (VIa), the mode C reaction product, was isolated. In the former instance VIa was isolated in 92% yield. Thus while VIa undoubtedly is formed much more readily from 1,1-diphenyl-3-benzylurea than from 1,1-diphenyl-4-benzylsemicarbazide, its isolation in both experiments precludes the identification of mode A or mode B reactions as the *sole* precursors to the mode C processes.[13]

Two experiments were performed to evaluate the effects of temperature variation. Thus when the reaction of Ic with morpholine was repeated, this time at room temperature and with a reaction time of 10 days, a 44% yield of 1-(N,N-diphenylcarbamyl)-morpholine (Va) was isolated *without the detection of any morpholino substituted semicarbazide (IVc)*. This latter compound was of course the major product formed when the reaction was conducted at reflux temperature. A similar result was obtained when Ic was dissolved in an excess of benzylamine, and the solution was then allowed to stand at ambient temperatures for 24 days. On work-up an 80% yield of 1,1-diphenyl-3-benzylurea was obtained together with a trace (<0.1%) of VIa. Thus with benzylamine, all 3 modes of reaction of Ic, *viz.*, A, B and C, have been realized by appropriate temperature control. It can be concluded from these temperature studies that the relative activation energies for the 3 modes of reaction of Ic, with an unhindered base as reaction medium, are as follows: mode C > mode A > mode B.

Some other aminolyses of Ic have been effected, again with the base employed as sole solvent, but in these instances either the mechanism involved or the total product identification is still unclear. For example, hydrazine hydrate[11a] (120°, 8.0); instead of yielding the anticipated (group a type) product, *viz.*, 4,4-diphenylsemicarbazide with Ic instead gave an 83% yield of diphenylamine. However, 4,4-diphenylsemicarbazide itself readily undergoes elimination,[14] when refluxed in an excess of hydrazine hydrate, to give diphenylamine in quantitative yield. The product from a Curtius rearrangement of Ic in hydrazine, *viz.*, 1,1-diphenylcarbohydrazide (IVf), can also yield diphenyl-

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(13) *Vide* E. Jolles and G. Ragni, *Gazz. chim. ital.*, **68**, 516 (1938); O. Bayer, *Z. angew. Chem.*, **59**, 257 (1947); F. Rekker, A. C. Faber, D. H. E. Tom, H. Verleur and W. Th. Nauta, *Rec. trav. chim.*, **70**, 163 (1951).

(14) *Cf.* F. L. Scott, A. Ahearne and J. Reilly, *J. Org. Chem.*, submitted for publication.

amine[15] and therefore the reaction of Ic with this nucleophile must remain anomalous. A similar situation exists with *n*-hexylamine[11a] (130°, 10.5). Its reaction with Ic does yield the expected (group b) derivative 1,1-diphenyl-4-*n*-hexyl semicarbazide, although in low yield (32%). This was accompanied, however, by a substance, isolated as a picrate, of formula $C_{15}H_{23}N_5O_8$, whose structure is still unknown. The reaction of Ic with β-(3,4-dimethoxyphenyl)-ethylamine[11a] (173° (26 mm.), *ca.* 10.0) resulted merely in the extensive formation of tars.

A slight possibility was considered that in the reactions of the group b amines, a preliminary Ar_2-5 cyclization,[16] akin to that observed with Ic and its congeners in boiling toluene or xylene,[7] might competitively cause the isocyanate II′ to close to indazolone III rather than aminate directly. In turn III would then re-open to form derivatives of type IV. Accordingly III was prepared and treated with both aniline and benzylamine under the standard aminolytic conditions used with Ic. In each case III was recovered in at least 80% yield. In addition no formation of III was detected in any of the aminolytic experiments conducted with Ic. The intermolecular amination of II′ is therefore much more rapid under the cited conditions than its possible intramolecular Ar_2-5 closure.

Experimental[17]

Diphenylcarbamyl azide (Ic) was prepared by the method of Stolle,[7a] *viz.*, by the reaction of diphenylcarbamyl chloride and sodium azide, in aqueous ethanol. After recrystallization from absolute ethanol, it was obtained as a white, microcrystalline solid, m.p. 75–76°, reported m.p.'s 78–79°[18] and 86°.[7a] The yields over numerous runs averaged between 75 and 80%.

Aminolyses of Ic in Ethanol. (i) Without Added Base.—On refluxing Ic in absolute ethanol for 723 hr. 1,1-diphenyl-2-carbethoxyhydrazine was formed in 90% yield. After crystallization from absolute ethanol it had a m.p. of 139–140°, reported[7a] m.p. 141°.

Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.3; H, 6.25; N, 10.9. Found: C, 70.5; H, 6.1; N, 11.2.

(ii) In the Presence of Amines.—When one equivalent of, *e.g.*, aniline, phenylhydrazine or piperidine was refluxed with an equimolar proportion of Ic for 1-hr. periods in ethanolic solution, unreacted Ic was recovered in each instance, in from 90–95% yield. When the reflux period was extended to 6 hr., more extensive reaction was detected. The following is typical of the reactions then observed. To 1.19 g. of Ic, dissolved in 20 ml. of ethanol, was added one equivalent (0.6 ml.) of cyclohexylamine, dissolved in 10 ml. of the same solvent. The solution was then refluxed for 6 hr. After standing at room temperature for a further 16-hr. period, white needles (180 mg., 11.7%), m.p. 197–200°, separated. These after further crystallization from ethanol had a m.p. of 202–203° and corresponded to 1,1-diphenyl-4-cyclohexyl semicarbazide.

Anal. Calcd. for $C_{19}H_{23}N_3O$: C, 73.8; H, 7.4; N, 13.6. Found: C, 73.9; H, 7.6; N, 14.1.

The initial filtrate on evaporation in a stream of air gave 1.04 g. (87%) of unreacted Ic. Under identical conditions, aniline resulted in a 65% recovery of Ic and a 17.2% yield of 1,1,4-triphenyl semicarbazide of m.p. 205–206°, reported[19] m.p. 206–207°.

Anal. Calcd. for$C_{19}H_{17}N_3O$: C, 75.2; H, 5.6; N, 13.9. Found: C, 74.8; H, 5.6; N, 14.4.

Approximately the same yields, *i.e.*, 15%, of the IV type compounds were obtained when the amines employed, again with a 6-hr. reflux period, were benzylamine and *n*-hexylamine. When the reflux period was increased to 46 hr. in the benzylamine reaction, the yield of 1,1-diphenyl-4-benzyl semicarbazide formed rose to 52%. The properties of the respective semicarbazides are included in Table I.

(b) Reaction of Ic, in Pyridine. (i) Without Any Other Added Base.—To 1.19 g. of Ic was added 5 ml. of redistilled, dry pyridine. The greenish-yellow solution thus obtained was then refluxed for 1 hr., during which time its color changed to a dark reddish-brown. The solution was then halved. The first half was diluted with water and a yellow oil separated which on the addition of a little alcohol solidified to a cream-colored solid, m.p. 150–159° (160 mg.). On repeated careful fractional crystallization from aqueous ethanol, two solids eventually were isolated. One consisted of white needles, m.p. 164–165° (50 mg.), and the other was a white amorphous solid (90 mg.), m.p. 237–239°. This latter substance, on further crystallization, had a m.p. of 244° and proved to be 1,1,5,5-tetraphenylcarbohydrazide (IVa), reported[7a,19] m.p. 239°, 242°.

Anal. Calcd. for $C_{25}H_{22}N_4O$: C, 76.2; H, 5.6; N, 14.2. Found: C, 75.6; H, 5.4; N, 13.9.

As had been reported previously, it slowly turned blue on exposure to air and light. The solid of lowest m.p., which had not been previously reported, has not yet been identified.

Anal. Calcd. for $C_{19}H_{24}N_3O$: C, 73.5; H, 7.7; N, 13.5. Found: C, 73.8; H, 7.9; N, 13.0.

The second half of the original solution afforded, after a further 2-hr. refluxing, 540 mg. of the cream-colored solid. On similar crystallization, this was again found to consist of the above two solids, in the ratio of 2:1 in favor of IVa.

(ii) In the Presence of Amines.—High yields (*ca.* 80%) of this latter substance were also obtained when equimolar quantities of Ic and either 5-aminotetrazole monohydrate or semicarbazide hydrochloride were again refluxed in pyridine as solvent for 1 hr. periods. Aniline, on the other hand, when analogously reacted yield 83% of 1,1,4-triphenyl semicarbazide. The following reaction illustrates the general aminolysis employed in this solvent. To 1.2 g. of β-naphthylamine, dissolved in 200 ml. of pyridine, was added 2.0 g. of Ic. The mixture was refluxed for 1 hr. and then allowed to cool to room temperature. To the reaction liquor was added 200 ml. of water and 2.39 g. (80%) of material, m.p. 216–220°, separated. A further 100 ml. of water added to the filtrate produced no added precipitation. Ethereal extraction of the diluted filtered solution, followed by separate evaporation of the aqueous and ethereal liquors, afforded no further appreciable quantity of product. After purificaton of the solid deposited, from ethanol, it corresponded to 1,1-diphenyl-4-β-naphthyl semicarbazide, m.p. 224°.

Anal. Calcd. for $C_{23}H_{19}N_3O$: C, 78.2; H, 5.4; N, 11.9. Found: C, 77.6; H, 5.1; N, 12.1.

The reactions in pyridine were roughly 50 times faster than the corresponding changes in ethanol, as measured by the extent of product formation.

(c) Reactions of Ic in Amines as Solvents.—The following examples are typical, respectively, of the three groups (of reactions) encountered. (1) To 1.19 g. of Ic was added 4.08 ml. of pyrrolidine; and the mixture was vigorously refluxed for 1 hr. On cooling, a white solid (620 mg.), m.p. 122–124°, separated. After recrystallization from aqueous ethanol, this was obtained as white needles, m.p. 123–124°, and proved to be 1-(N,N-diphenylcarbamyl)-pyrrolidine (Vc).

Anal. Calcd. for $C_{17}H_{18}N_2O$: C, 76.7; H, 6.8; N, 10.5. Found: C, 76.7; H, 6.8; N, 10.5.

A further quantity (520 mg.) of Vc was obtained from the reaction-liquor filtrate on evaporation and work-up; the total yield was 86%.[20]

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[15] Compare F. D. Chattaway and M. Aldridge, *J. Chem. Soc.*, **99**, 407 (1911); E. Fischer, *Ann.*, **190**, 175 *et seq.*, (1878); H. Wieland and E. Wecker, *Ber.*, **43**, 3265, 3269 (1910).

[16] *Cf.* S. Winstein, R. Heck, S. Lapport and R. Baird, *Experientia*, **12**, 138 (1956).

[17] All melting points are uncorrected. All microanalyses are by Drs. Weiler and Straus, Oxford, England.

[18] B. Toschi, *Gazz. chim. ital.*, **44**, I, 447 (1914).

[19] S. F. Acree, *Ber.*, **36**, 3157 (1903).

[20] The yields cited in this, and the other aminolyses, are generally reproducible to only within ±5%. This factor may be even somewhat larger when several products are involved. That the error involved is of this order is due mainly to inherent difficulty in work-up of the

TABLE I

SOME AMINOLYSIS PRODUCTS OF DIPHENYLCARBAMYL AZIDE

Amine[a]	Product	Formula	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Allylamine	1,1-Diphenyl-3-allylurea[b]	$C_{16}H_{16}N_2O$	75–76	60	76.2	75.9	6.3	6.3	11.1	11.4
n-Decylamine	1,3-Di-*n*-decylurea[c]	$C_{21}H_{44}N_2O$	94–95	90	74.1	73.5	12.9	13.2	8.2	8.5
Furfurylamine	1,1-Diphenyl-4-furfuryl semicarbazide[d]	$C_{18}H_{17}N_3O_2$	195	75	70.4	70.0	5.5	5.7	13.7	14.1
n-Hexylamine	1,1-Diphenyl-4-*n*-hexyl semicarbazide	$C_{19}H_{25}N_3O$	125–127	32	73.3	73.3	8.0	7.9	13.5	14.1
n-Hexylamine	Unidentified[e]	$C_{15}H_{23}O_8N_5$	122–123	..[f]	45.0	44.5	5.8	5.6	17.5	17.4
Isopropylamine	1,1-Diphenyl-4-isopropyl semicarbazide	$C_{16}H_{19}N_3O$	189–190[g]	6[h]	71.4	72.0	7.1	7.4	15.6	15.4
Morpholine	1-(N,N-Diphenylcarbamyl)-morpholine[i]	$C_{17}H_{18}N_2O_2$	106–107[j]	4[k]	72.3	72.5	6.3	6.6	9.9	10.0
Morpholine	Morpholine-4-carboxylic acid, N,N-diphenylhydrazide[l]	$C_{17}H_{19}N_3O_2$	232–233	72	68.7	69.2	6.4	6.8	14.1	14.2
4-Ethoxyaniline	1,3-Di-(*p*-ethoxyphenyl)-urea[m]	$C_{17}H_{20}N_2O_3$	225–227	71	68.0	67.7	6.7	7.0	9.3	9.2
β-Phenylethylamine	1,3-(Di-(β-phenylethyl)-urea[n]	$C_{17}H_{20}N_2O$	135–137[o]	42	76.1	76.1	7.5	7.5	10.4	10.6
Piperidine	1-(N,N-Diphenylcarbamyl)-piperidine[p]	$C_{18}H_{20}N_2O$	108–110[q]	92	77.1	77.2	7.1	6.9	10.0	10.4

[a] All reactions summarized herein were conducted with an amine to azide ratio of 10:1, without additional solvent other than the base employed and at the boiling point of the respective amine. All reaction times correspond to 1 hr. reflux, save with isopropylamine, whose reaction period was 45 minutes. [b] This was accompanied by an oily contaminant which was not further investigated. [c] Considerable quantities of *n*-decylammonium *n*-decyl carbamate, m.p. 85°, formed by aerobic N-carboxylation of the amine environment were also detected. Compare ref. 20. [d] This substance is IVd. [e] The analytical, and other, data are for a picrate salt. [f] A 480-mg. quantity of picrate was obtained from the reaction of 1.19 g. of Ic and 6.3 ml. of *n*-hexylamine. [g] Reported m.p. 193°, by C. C. P. Pacilly, *Rec. trav. chim.*, **55**, 120 (1936). [h] An 80% yield of unreacted Ic was also recovered. [i] This is Va. [j] Reported m.p. 110–111° (cor.), by R. A. Henry and W. M. Dehn, THIS JOURNAL, **72**, 2806 (1950). [k] The yield of Va obtained at room temperature has been discussed earlier. [l] This represents IVc. [m] Represented by VIc. [n] Corresponds to VId. [o] M.p. 140–141°, as reported by N. I. Moyer and W. E. McEwen, *ibid.*, **73**, 3075 (1951). [p] Corresponds to Vb. [q] T. W. Evans and W. M. Dehn, *ibid.*, **52**, 3646 (1930), record this m.p. as 110°.

(2) Analogously reacted, and with similar work-up, a ninefold excess of refluxing pyrrole afforded, together with a trace (<1%) of what may be 1-(N,N-diphenylcarbamyl)-pyrrole (Vd), a (total) 84% yield of the N,N-diphenylhydrazide of pyrrole-1-carboxylic acid (IVb), as a fine white powder, m.p. 230–231°.

Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.6; H, 5.4; N, 15.2. Found: C, 73.6; H, 5.4; N, 15.2.

(3) After 6 ml. of cyclohexylamine had been added to 1.19 g. of Ic, the mixture was refluxed for 60 minutes, during which time white fumes were evolved vigorously. On standing for 16 hr. a solid (1.0 g., 65%), m.p. 195–197°, deposited, which crystallized from ethanol as white needles, m.p. 202–203°, and which did not depress the m.p. of 1,1-diphenyl-4-cyclohexyl semicarbazide prepared as above. The filtrate on evaporation and work-up yielded another white solid (900 mg.), m.p. 150–158°. This after recrystallization from ethanol was obtained as white needles (600 mg., 35%), m.p. 185–186°, and corresponded to 1,1-diphenyl-3-cyclohexylurea.

Anal. Calcd. for $C_{19}H_{22}N_2O$: C, 77.6; H, 7.5; N, 9.5. Found: C, 77.6; H, 7.4; N, 9.5.

(4) During the refluxing of a mixture of 5.4 ml. of benzylamine and 1.19 g. of Ic, for 1 hr., a yellow coloration slowly developed and white fumes were briskly evolved. On cooling, a white crystalline solid (1.32 g.), m.p. 125–135°, separated. By fractional crystallization from aqueous ethanol, two solids were separated from the mixture, one as fine white needles, m.p. 200–202° (450 mg.), the other as cream-colored needles, m.p. 150–152° (550 mg.). The higher melting solid after further purification from ethanol was obtained again as long needles, m.p. 202–204°, and corresponded to 1,1-diphenyl-4-benzyl semicarbazide, yield 28%.

Anal. Calcd. for $C_{20}H_{19}N_3O$: C, 75.7; H, 6.0; N, 13.2. Found: C, 75.6; H, 6.4; N, 13.7.

The lower melting fraction, after further purification, was also obtained as white needles, m.p. 162–164°. This was symmetrical dibenzylurea (VIa), reported[21] m.p. 165–167°. It did not depress the m.p. of an authentic sample.[22]

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 75.0; H, 6.6. Found: C, 74.9; H, 6.6.

The initial filtrate on evaporation in a stream of air gave a further quantity of VIa; total yield thereof obtained was 50%.

This reaction was repeated without refluxing the mixture. Instead it was allowed to stand at room temperature for 24 days. After such standing a trace (<0.1%) of VIa separated as needles from the solution and on work-up of the mother liquor an 86% yield of 1,1-diphenyl-3-benzylurea, together with some benzylammonium benzyl carbamate, was isolated. The majority of the remaining aminolyses conducted in amine type solvents are summarized in Table I.

Some Cognate Observations.—(A) When similarly treated with Ic, without further solvent, an excess (ninefold) of hydrazine hydrate resulted in an 83% yield of diphenylamine. For some comments on this total deacylation, see the discussion above. (B) A ninefold excess of *n*-amylamine gave with Ic an 81% yield of 1,1-diphenyl-3-*n*-amylurea, m.p. 70–71°, identified by mixed melting point with an authentic sample.[23] (C) When 1,1-diphenyl-3-benzylurea was refluxed in an excess of benzylamine for 1 hr., it formed 1,3-

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amine liquors, in some of which, for example, there is an inevitable complication due to carbonation of the basic medium to form crystalline ammonium carbamates. See, *e.g.*, H. B. Wright and M. B. Moore, THIS JOURNAL, **70**, 3865 (1948).

(21) P. P. Grad and R. J. Dunn, *Anal. Chem.*, **25**, 1211 (1953).

(22) All the symmetrical disubstituted ureas obtained in the present work from the group c amine reactions with Ic were also unambiguously synthesized by the reaction of urea and the appropriate amine, with 1 hr. reflux, in the absence of any further solvent. This latter technique yielded the VI type derivatives in quantitative yield. In each case, samples of the appropriate VI derivative prepared by the unambiguous route just mentioned and by the mode C route of the present work did not depress, on mixture m.p.

(23) Prepared by the reaction of diphenylcarbamyl chloride and *n*-amylamine in pyridine and by the method of Scott, Ahearne and Reilly, ref. 14.

dibenzylurea (VIa) in 92% yield. When 1,1-diphenyl-4-benzyl semicarbazide was similarly treated, it was recovered in *ca.* 60% yield and 20% VIa was isolated. Both reaction products were heavily contaminated with benzylammonium benzyl carbamate. (D) The attempted aminolysis of Ic with β-(3,4-dimethoxyphenyl)-ethylamine resulted merely in extensive tar formation and was not further pursued. (E) Some color reactions analogous to those described by Dewey and Gelman[24] were attempted with representative IV, V and VI compounds, with a view to the development of a possible distinguishing test. The colors were (a) first developed in concentrated sulfuric acid solution and then (b) modified by the addition of a few drops of a 1% aqueous sodium nitrate solution.[25] The following summarizes the color transitions observed: with IVa, IVb, IVc and the corresponding 1,1-diphenyl-4-benzyl-, -4-cyclohexyl and -4-*n*-hexyl semicarbazides, deep blue to dark brown; with 1,1,4-triphenylsemicarbazide merely intensification of the original deep blue color and with the isomeric 1,4,4-triphenyl semicarbazide a shift from pink to green; with VIa and the corresponding 1,1-diphenyl-3-allyl- and -3-benzyl-ureas, yellow-green to orange-brown; with IVe blue to green; and Va, Vb and Vc, a blue to green, a colorless to green and blue to brown halochromism was observed, respectively.[26] As can be seen, the colors and color changes encountered were too diverse to reveal any systematic variation. (F) 1-Phenyl-2-indazolone (III) was prepared by Stolle's method.[7a] When III was refluxed for 1 hr. in a ninefold excess of aniline or benzylamine, it was recovered in 80 and 82% yields, respectively. (G) For convenience we append together at this point a trio of phenylhydrazine aminolyses. (1) To 1.19 g. of Ic was added 9.0 ml. (an approximately 20 molar proportion) of phenylhydrazine. The solution was then refluxed for 1 hr. and poured, when cooled, into an excess of water. A white solid (850 mg., 53%), m.p. 154–157°, was obtained on working up the yellow viscous oil initially precipitated. After recrystallization from absolute ethanol, this was obtained as white needles, m.p. 167–168°. This was most probably a triphenyl carbohydrazide,[27] the 1,1,5-isomer rather than the 1,1,4-derivative.

Anal. Calcd. for $C_{19}H_{18}N_4O$: C, 71.7; H, 5.7; N, 17.6. Found: C, 71.1; H, 5.6; N, 17.2.

Some excess phenylhydrazine was recovered on ethereal extraction of the aqueous mother liquor but no further quantity of solid. (2) To 1.16 g. of diphenylcarbamyl chloride, dissolved in 5 ml. of dry pyridine, was added 0.45 ml. of phenylhydrazine. The solution was then refluxed for 30 minutes, poured into water and the oil obtained, which rapidly solidified, on working up with 95% aqueous ethanol gave light yellow crystals, m.p. 145–147° (230 mg., 15%). These were obtained on further crystallization as white crystals, m.p. 148–149°.

Anal. Calcd. for $C_{19}H_{17}N_3O$: C, 75.2; H, 5.6; N, 13.9. Found: C, 74.8; H, 5.7: N, 14.4.

These correspond to 1,4,4-triphenyl semicarbazide, reported[28] m.p. 151–152°. Incidentally, the other possible isomer, *viz.*, 2,4,4-triphenyl semicarbazide, has been reported[29] to melt at 124–125°. The poor yield of the former isomer isolated does nothing to discount the possibility of the latter derivative also being present but undetected.[30] The aqueous filtrate was evaporated and left an oily residuum, from which a trace of solid was obtained. This on treatment with ethanol and water gave a precipitate, m.p. 240–243°. Insufficient quantities were obtained for further study. (3) When reaction number 2 was attempted under different conditions, *viz.*, with 1.16 g. of diphenylcarbamyl chloride dissolved in 4.5 ml. of phenylhydrazine, 1 hr. refluxing resulted in a vigorous evolution of white fumes from the reaction liquor and a deposition of 550 mg. of solid, m.p. 220–222°, on cooling. This after crystallization from aqueous ethanol was obtained as a fine microcrystalline substance, m.p. 225–226°,[31] which turned slightly pink on exposure to air.

Anal. Calcd. for $(C_{13}H_{12}N_2O)_x$: C, 73.6; H, 5.7; N, 13.2. Found: C, 73.1; H, 5.8; N, 13.2.

(H) Some Aminolyses of Diphenylcarbamyl Chloride.—The reaction with benzylamine typifies the general procedure adopted. To 1.16 g. of diphenylcarbamyl chloride in 5 ml. of anhydrous pyridine was added 0.54 ml. of benzylamine. The solution was then refluxed for 30 minutes during which time a dark red color developed therein. It was then poured into an excess of ice-water and on standing a yellow solid (850 mg.), m.p. 101–104°, separated. Recrystallization from aqueous ethanol, using a little Norite, afforded the 1,1-diphenyl-3-benzylurea as white needles, m.p. 104–105°, reported[32] m.p. 104–106°.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.5; H, 6.0; N, 9.3. Found: C, 79.5; H, 6.0; N, 9.0.

A further quantity (40 mg.) of this substance was obtained from the filtrate on work-up; total yield 59%. Morpholine similarly reacted afforded a 71% yield of Va as white crystals, m.p. 107–108°, which did not depress the melting point of a sample of Va, prepared by the morpholine aminolysis of Ic, as further detailed in Table I. Similarly, cyclohexylamine afforded a 57% yield of 1,1-diphenyl-3-cyclohexylurea analogously recognized. With pyridine itself, the only solid isolated was its addition complex with diphenylcarbamyl chloride, m.p. 111–113°, reported[33a] m.p. 107°, m.p. 110°.[33b]

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(24) B. T. Dewey and A. H. Gelman, *Ind. Eng. Chem., Anal. Ed.*, **14**, 361 (1942).

(25) Compare the reaction of diphenylamines and nitrous ion, N. V. Sidgwick, T. W. J. Taylor and W. Baker, "The Organic Chemistry of Nitrogen," Oxford University Press, Oxford, England, 1945, pp. 62, *et seq.*

(26) The color shifts recorded are those encountered in the shift of conditions from a to b.

(27) It is interesting to note that the observed melting point is within the range recorded for 1-phenyl semicarbazide and its complex with *sym*-diphenyl carbazide, see C. R. Noller, THIS JOURNAL, **52**, 1132 (1930). However, this formulation for the solid obtained in the present experiment is not supported by its microanalytical data. On the whole, because of the general uncertainty of the melting point criterion as indicated by Noller, we base our provisional identification on the analytical information.

(28) E. Jolles and B. Bini, *Gazz. chim. ital.*, **68**, 510 (1938).

(29) G. H. Coleman, H. Gilman, C. E. Adams and P. E. Pratt, *J. Org. Chem.*, **3**, 99 (1938).

(30) See R. A. Henry, S. Skolnik and G. B. L. Smith, THIS JOURNAL. **75**, 955 (1953), and particularly ref. 10 therein, for some interesting data on cognate substituted hydrazine acylations.

(31) Jolles and Ragni, ref. 13, noted that N,N-methylphenylurea when heated with phenylhydrazine at 185–190° for 30 minutes resulted in the formation of 1,5-diphenylcarbohydrazide, together with a small quantity of solid, m.p. 225°; this on the basis of a nitrogen analysis (Found: N, 24.66), they suggested might be $NH(CONHNHC_6H_5)_2$ (calcd.: N, 24.56).

(32) S. Kushner, R. I. Cassell, J. Morton and J. H. Williams, *J. Org. Chem.*, **16**, 1283 (1951).

(33) (a) E. V. Meyer and A. Nicolaus, *J. prakt. Chem.*, **82**, 521 (1910); (b) J. Herzog, *Ber.*, **40**, 1832 (1907).