tionality between $\Delta S°$ and $\Delta G°$ that has been observed for many acids, and accounts for the absence of correlation between $\Delta S°$ and $\Delta C_p°$.

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The Preparation of 1,1-Diarylhydrazines

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In connection with some other work, pure 1,1-diphenylhydrazine was required in fairly large quantities. Although several routes are available for the preparation of 1,1-disubstituted dialkyl- and aralkylhydrazines, the reduction of the corresponding N-nitrosamine is practically the only general method for the synthesis of 1,1-diarylhydrazines.[1b]

In spite of its apparent relative simplicity, the reduction of 1,1-diphenylnitrosamine is always attended by cleavage of the N–N bond and the formation of diphenylamine.[2] The crude reaction product is usually a highly colored mixture of diphenylamine and of the desired hydrazine. The tedious purification yields more often than not 1,1-diphenylhydrazine hydrochloride as pale violet or silvery gray crystals at best, and, unless the purification is carried out carefully, substantial losses of product occur.

The experimental difficulties coupled with the rather prohibitive price of the commercial product (which is not pure) prompted us to investigate other routes to 1,1-diphenylhydrazine. One of the methods for the preparation of primary amines is the group of reactions which includes the Schmidt, the Hoffmann, and the Curtius rearrangement. Diaryl- and aralkylcarbamyl azides rearrange to give the corresponding N-isocyanates. Although this reaction has not been widely investigated,[3] the report by Scott and Scott[4] that 1,1-diphenylcarbamyl azide underwent the Curtius rearrangement in ethanol encouraged us to evaluate this as a potentially very useful and clean method to prepare 1,1-diarylhydrazines.

Three factors were of importance: high yields, ease of operations, and the purity of the hydrazines. Although it is known that primary alkyl esters of carbamates are difficult to hydrolyze, the hydrolysis of ethyl 3,3-diphenylcarbazate[4] (III, Ar = Ph, $R = C_2H_5$–) was attempted under both acidic and basic conditions; in both cases the ester was recovered unchanged. However, the *t*-butyl ester (III, Ar = Ph, R = *t*-Bu–), in addition to the advantage of a shorter time for its preparation, was hydrolyzed easily to 1,1-diphenylhydrazine hydrochloride (IV·HCl) in 98% yield.

$$\underset{\text{I}}{Ar_2NCOCl} + NaN_3 \longrightarrow \underset{\text{II}}{Ar_2NCON_3} \xrightarrow{ROH} \underset{\text{III}}{Ar_2NNHCO_2R} \xrightarrow{H_2O} \underset{\text{IV}}{Ar_2NNH_2}$$

In order to evaluate its practical value for the preparation of 1,1-diphenylhydrazine, the sequence was carried through without purification of the intermediates. Thus, diphenylcarbamyl azide (II, Ar = Ph), mp 65°, obtained in 97% yield from the reaction of diphenylcarbamyl chloride and sodium azide, was heated under reflux with *t*-butyl alcohol for 5 days. The reaction was monitored by infrared spectroscopy and *t*-butyl 3,3-diphenylcarbazate (not isolated) was hydrolyzed with concentrated hydrochloric acid. 1,1-Diphenylhydrazine hydrochloride was obtained in 78% yield as *colorless* needles. Pure, *white* 1,1-diphenylhydrazine was isolated in 89% yield from its hydrochloride. The over-all yield of *pure* 1,1-diphenylhydrazine from diphenylcarbamyl chloride was 66%. In order to test the generality of this method, N-aminocarbazole was prepared and obtained as a pure solid in 74% yield (over-all) from biphenylenecarbamyl chloride.

Except in cases when groups which are sensitive to the reagents used are present, this procedure should prove to be a widely useful method for the preparation of pure 1,1-diarylhydrazines. Although the decomposition of the azides and the subsequent reaction of the N-isocyanates with *t*-butyl alcohol takes about 5 days to be completed, the esters are stable and can be prepared in large quantities. The simple hydrolysis of the ester affords the pure hydrazine hydrochlorides in high yields.

Experimental Section[5]

N,N-Diphenylcarbamyl Azide.—A mixture of 23.2 g (0.1 mol) of diphenylcarbamyl chloride and 200 ml of ethanol contained in a 500-ml, round-bottom flask equipped with a reflux condenser was heated to 60°. As soon as solution had occurred, a solution of 6.5 g (0.1 mol) of sodium azide in 20 ml of water was added. The reaction mixture was heated under reflux with stirring for 3 hr. The ethanol was evaporated and 20 ml of water was added to the residue. The aqueous mixture was extracted with two 100-ml portions of ether. The dried ether extract was evaporated to give 23 g (97%) of diphenylcarbamyl azide, mp 65°. This compound was pure enough for the rearrangement reaction.

1,1-Diphenylhydrazine Hydrochloride.—A solution of 23 g of diphenylcarbamyl azide in 150 ml of *t*-butyl alcohol was heated under reflux for 5 days. After that time, the azide band (at 2160 cm^{-1}) had completely disappeared. A white solid, which was shown to be tetraphenylcarbohydrazide, mp 238°, by its infrared spectrum and a mixture melting point, was filtered. To the filtrate was added 10 ml of concentrated hydrochloric acid and the solution was heated under reflux for 3.5 hr. The residue left after removal of the solvent was washed with 50 ml of ether, and 1.3 g of *t*-butyl 3,3-diphenylcarbazate was obtained. The ether-insoluble *white* solid proved to be 1,1-diphenylhydrazine hydrochloride, mp 165–170°, and weighed 16.6 g (78%).

1,1-Diphenylhydrazine.—The hydrazine hydrochloride (19.3 g) obtained from the above procedure was dissolved in 500 ml of hot water and made strongly alkaline with 20 ml of a 7.5 *N* aqueous sodium hydroxide solution. The free hydrazine was

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then extracted with three 50-ml portions of ether. The solvent was stripped from the dried ether (potassium carbonate) and the residue was distilled to give 14.3 g (89%) of pure 1,1-diphenylhydrazine, bp 120° (1.1 mm). Its hydrazone with *p*-nitrobenzaldehyde melted at 131–132° (lit.[6] mp 131°).

A solution of 10.2 g (0.036 mol) of *t*-butyl 3,3-diphenylcarbazate in 100 ml of methanol containing 5 ml of concentrated hydrochloric acid was heated under reflux for 3 hr. Work-up as above gave 7.7 g (98%) of 1,1-diphenylhydrazine hydrochloride, mp 165–170°. Attempted hydrolysis of this ester under strongly alkaline conditions was ineffective. Ethyl 3,3-diphenylcarbazate was formed in 97% yield after 15 days of reflux of a solution of 15 g of diphenylcarbamyl azide. (Reference 4 does not give the amounts used when 30 days were required to complete the reaction.)

***t*-Butyl 3,3-Diphenylcarbazate.**—A solution of 22.1 g (0.09 mol) of diphenylcarbamyl azide, mp 65°, in 150 ml of *t*-butyl alcohol and 50 ml of toluene was heated under reflux for 5 days. Removal of the solvent left 25 g (92%) of *t*-butyl 3,3-diphenylcarbazate. One recrystallization from cyclohexane gave 20.4 g (76%) of product, mp 122.5–124°.

Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.83; H, 7.04; N, 9.87. Found: C, 71.57; H, 7.54; N, 9.93.

Biphenylenecarbamyl Azide.—The procedure used for the preparation of diphenylcarbamyl azide gave 39 g (98%) of biphenylenecarbamyl azide, mp 92–93°, from 39 g of carbamyl chloride.

Anal. Calcd for $C_{13}H_8N_4O$: C, 66.09; H, 3.41; N, 23.72. Found: C, 65.91; H, 3.57; N, 22.92.

***t*-Butyl 3,3-Biphenylenylcarbazate.**—A solution of 39.0 g (0.16 mol) of biphenylenecarbamyl azide in 200 ml of *t*-butyl alcohol and 50 ml of toluene was heated under reflux for 10 days. Upon cooling, 4.5 g of white silky solid precipitated, mp >300°. This is probably bis(biphenylenyl)carbohydrazide. Removal of the solvent left 38 g (82%) of the ester, mp 120–122°.

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.31; H, 6.42; N, 9.92. Found: C, 72.86; H, 6.38; N, 9.80.

N-Aminocarbazole Hydrochloride.—A solution of 38.0 g (0.13 mol) of *t*-butyl 3,3-biphenylenylcarbazate in 200 ml of methanol containing 18 ml of concentrated hydrochloric acid was heated under reflux for 5 hr. Removal of the solvent left a white solid which was washed with 100 ml of ether. N-Aminocarbazole hydrochloride was obtained (28.5 g, 97%) as silky white crystals, mp 155–156° (dec).

N-Aminocarbazole.—A suspension of 28.5 g (0.13 mol) of N-aminocarbazole hydrochloride in 200 ml of water was made strongly alkaline by the addition of 10 g of sodium hydroxide. The solution was then extracted with two 200-ml portions of ether. Evaporation of the dried ether extract (potassium carbonate) and recrystallization of the residue from ethanol gave 22.7 g (96%) of pale tan needles, mp 147–148°. Its N-benzoyl derivative melted at 230–231° (lit.[7] mp 231–232°).

Registry No.—II, Ar = Ph, 17223-83-5; III, Ar = Ph; R = *t*-Bu, 17223-84-6; IV, Ar = Ph, 530-50-7; IV, Ar = Ph·HCl, 530-47-2; biphenylenecarbamyl azide, 17255-74-2; *t*-butyl 3,3-biphenylenylcarbazate, 17223-87-9; N-aminocarbazole hydrochloride, 17223-86-8; N-aminocarbazole, 17223-85-7.

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Bond Deformations in Conjugated Molecules

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Frequent attempts have been made to evaluate the geometries of conjugated molecules *via* utilization of bond-order–bond-length relationships.[1] In a recent examination, the possible inadequacy of this approach was noted for the nonalternant molecule, fluoranthene.[2] For this system, consideration of the underlying σ network leads to a significantly different calculated structure.

The effects of such σ strain on the π energies of cyclic conjugated systems have been considered by Gleicher[3] and by Allinger and his coworkers.[4,5] In these studies attention was particularly focused on possible deviations from planarity of certain nonalternant molecules.

Discrepancies have been noted between experimentally obtained bond lengths and those calculated from bond orders for alternant hydrocarbons. It would be attractive to explain these differences as due to a similar relief of strain-producing factors. In these systems angle strain represents a near-negligible factor. The chief driving force toward possible bond deformation would be to reduce the strain associated with severe nonbonded interactions. To test this, a series of polycyclic systems related to phenanthrene was chosen for study. Bond deformations have been considered as energetically ineffective means of relieving molecular strain.[6] The relatively small changes in bond length treated here, however, do lead to an observable decrease in strain. All of the molecules studied were assumed to be planar. The complexity of including out-of-plane motions was felt to be prohibitive even though such calculations have previously appeared.[7]

The following approach was utilized. A trial structure was constructed from bond lengths based on SCF-MO bond orders.[8] A minimum strain energy was then found by systematically varying the coordinates of the atoms.[9,10] As in earlier work from this laboratory, the in-plane bending force constants and carbon–hydrogen stretching force constant were obtained from Cyvin's analysis of benzene[11] and the nonbonded interaction potentials from Bartell's study on intramolecular van der Waals forces.[12] The carbon–carbon stretching force constants were assumed to be a function of the bond length.[2] These were correlated by the relationship developed by Dewar and Schmeising.[13] Although attention is principally directed to long, easily deformable bonds, such as e–f in phenanthrene, Table I contains the values of all calculated and experimental bond lengths. The structures used appear in Chart I.

The unfavorable nonbonded interactions are least serious in phenanthrene. Minimization of the strain energy leads to a structure which differs only slightly from the starting geometry. Two bonds, a–i and h–i, the experimental values of which are unexpected, are not changed in this treatment.[14] It has been suggested

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