Indolization of the Phenylhydrazones. A solution of 4.0 g of the phenylhydrazone and 26 g of anhydrous $ZnCl_2$ in absolute ethanol was refluxed for 5 h. Water was added, and the mixture was made alkaline with sufficient sodium hydroxide to dissolve the $Zn(OH)_2$ precipitate and extracted with ether. The ether extracts were washed with 1.0 N HCl, water, and 10% $NaHCO_3$ and dried over Na_2SO_4. The ether was evaporated, and the indole was purified by vacuum distillation. *cis*-6a,10a-10a-Methyl-6,6a,7,8,9,10,10a,11-octahydro-5*H*-benzo[*b*]-carbazole (**7a**): bp 180–184 °C (1 mm); mp 44–46.5 °C; yield, 44%; UV max 229 nm (log ϵ 4.43), 284 (3.79), 291 (3.74); NMR δ 1.05 (CH_3); mass spectrum, *m/e* (relative intensity) 239 (30), 238 (4), 183 (9), 182 (15), 180 (10), 170 (4), 168 (16), 167 (18), 144 (20), 143 (100), 129 (10), 127 (8), 117 (5), 116 (4), 115 (12), 77 (14), 76 (4), 65 (6), 63 (5), 51 (8), 50 (3), 39 (23).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.35; H, 8.75; N, 5.86. Found: C, 85.43; H, 8.53; N, 5.44.

The same product was obtained by heating the phenylhydrazone in glacial acetic acid at 80 °C for 5 h (yield, 36%).

trans-6a,10a-10a-Methyl-6,6a,7,8,9,10,10a,11-octahydro-5*H*-benzo[*b*]carbazole (**7b**): bp 189–194 °C (1 mm); yield, 41%; UV max 228 nm (log ϵ 4.45), 284 (3.78), 291 (3.74); NMR δ 0.88 (CH_3); mass spectrum, *m/e* (relative intensity) 239 (69), 238 (10), 224 (7), 183 (8), 182 (13), 180 (9), 170 (7), 168 (12), 167 (12), 144 (32), 143 (100), 129 (12), 127 (6), 117 (3), 116 (3), 115 (7), 77 (7), 76 (2), 65 (3), 63 (4), 51 (4), 50 (1), 39 (3).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.35; H, 8.79; N, 5.86. Found: C, 84.96; H, 8.38; N, 5.46.

The same product was obtained by heating the phenylhydrazone in glacial acetic acid at 80 °C for 5 h (yield, 31%).

Mass Spectrum of 1,2,3,4-Tetrahydrocarbazole:[12] MS *m/e* (relative intensity) 171 (24), 170 (12), 114 (14), 143 (100), 129 (6), 127 (7), 117 (4), 116 (5), 115 (18), 77 (10), 76 (6), 65 (5), 63 (10), 51 (10), 50 (6), 39 (12).

Registry No.—**4a**, 938-06-7; **4a** phenylhydrazone, 66674-97-3; **4b**, 938-07-8; **4b** phenylhydrazone, 66674-98-4; **7a**, 66674-99-5; **7b**, 66675-00-1; 9-methyl-Δ^4-3-octalone, 826-56-2; phenylhydrazine, 100-63-0; 1,2,3,4-tetrahydrocarbazole, 942-01-8.

References and Notes

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(10) Melting points were taken on a Buchi melting point apparatus and are uncorrected. UV spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer in 95% ethanol solution. NMR spectra were determined in CCl_4 or $CDCl_3$ solution using internal Me_4Si on a Varian A60-A spectrometer. Mass spectra were measured with a Hitachi Perkin-Elmer RMU-6 instrument at 70 eV. Elemental analyses were performed by Mr. Jerry Darby using a Perkin-Elmer 240 analyzer.
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Reaction of Picryl Chloride with 3,5-Dinitrotriazole: Formation of 1-Picryl-3-nitro-5-chloro-1,2,4-triazole and 1-Picryl-3-nitro-1,2,4-triazol-5-one

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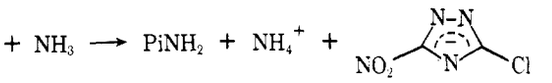
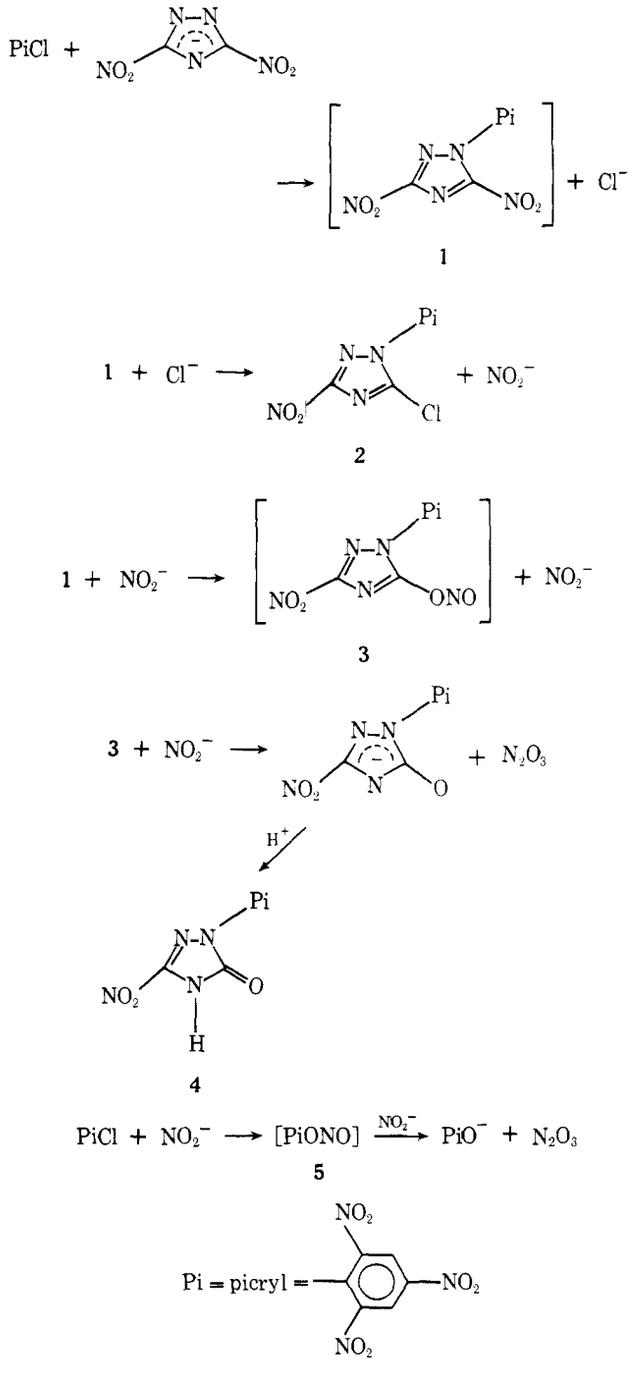
The reaction of picryl chloride with 3,5-dinitrotriazole salts (K^+, Li^+) in dry acetonitrile results in a complex mixture of products which include 1-picryl-3-nitro-5-chloro-1,2,4-triazole (**2**), 1-picryl-3-nitro-1,2,4-triazol-5-one (**4**), 2,4,6-trinitrophenol (picric acid), and oxides of nitrogen. The products (**2** and **4**) were identified by mass spectroscopy (parent ions), IR (characteristic bands for aromatic H; NH and C=O for **4**), NMR (singlets for picryl H; broad singlet (NH) for **4**), and elemental analysis. Additional evidence for the structure of **2** was its reaction with ammonia to give 2,4,6-trinitroaniline and ammonium chloronitrotriazole. Further support for the structures of **2** and **4** is that the formation of these products can be rationalized via the expected primary reaction intermediate, 1-picryl-3,5-dinitro-1,2,4-triazole (**1**) (see Scheme I).

Positional isomers for the intermediate **1** and compounds **2** and **4** are possible and the structures assigned to these species are the most likely ones based on previous structure



Scheme I



determinations for 3,5-dinitrotriazole reaction products. For example, methylation of 3,5-dinitrotriazole gives only the N_1-alkylation product, 1-methyl-3,5-dinitrotriazole (**6**), and no methylation at the N_4 position occurs even though a variety of methylating agents and reaction conditions were employed.[1] Similarly, reaction of 3,5-dinitrotriazole and its salts with epoxides[2] and allyl halides[3] gives the N_1-substituted products.[4] Thus the structures for **2** and **4** (and the intermediate **1**) were assigned with the picryl group attached to the N_1 position of the triazole ring.

The reaction of **6** with nucleophiles results in replacement of the nitro group in the 5 position of the triazole ring. Thus, heating **6** with aliphatic amines gives the respective 5-amino derivatives[5] and, under similar conditions, **6** with triethylamine in aqueous dioxane yields 1-methyl-3-nitro-1,2,4-triazol-5-one[5] and with concentrated hydrochloric acid yields 1-methyl-3-nitro-5-chloro-1,2,4-triazole.[6] Based on this evidence the displacement of the nitro group from **1** (resulting in the formation of **2** and **4**) was assumed to take place at the 5 position.

The following pathway for the reaction of picryl chloride with 3,5-dinitrotriazole salts seems plausible and accounts for the observed products. Attack of 3,5-dinitrotriazole anion on picryl chloride displaces chloride ion to give the intermediate product, 1-picryl-3,5-dinitro-1,2,4-triazole (**1**); chloride ion in turn displaces nitrite from **1** to give **2**; nitrite ion can then attack both **1** and starting picryl chloride to give **4** and picric acid, respectively, along with oxides of nitrogen (whose evolution is observed). The complexity of the overall reaction apparently results from an unusual concurrence of species being generated in the reaction: Although the nitro groups in the starting 3,5-dinitrotriazole anion are not labile, attachment of the picryl group to the triazole ring (**1**) sufficiently activates a nitro group to allow displacement by Cl^- generated from picryl chloride during the formation of **1**; the species (NO_2^-) displaced from **1** by chloride ion can attack the starting picryl chloride to produce the nitrite ester (**5**), a process which generates additional chloride ion; attack of nitrite ion on the initial product (**1**) to give **3** produces no net loss in nitrite ion but further reaction of nitrite with **3** (as well as with **5**) to form N_2O_3 gas irreversibly removes nitrite ion from the system (thereby driving any reversible reactions involving nitrite ions toward completion).

The reactions of **1** and picryl chloride with nitrite ion are analogous to the reactions of 1,2,4-trinitrobenzene and 2,4-dinitrohalobenzenes with nitrite to give 2,4-dinitrophenoxide and oxides of nitrogen.[7] In the reaction described here sufficient nitrite ion may not be available for complete conversion of the intermediate nitrite esters (**3** and **5**) to **4** and picric acid, but hydrolysis of **3** and **5** during workup would give the same products. Although it appears possible that **2** might hydrolyze to **4** during workup this was shown not to be the case. The hydrolysis of **2** in aqueous acetonitrile is quite slow and the products are picric acid and chloronitrotriazole.

The reaction of picryl chloride with 3,5-dinitrotriazole salts was monitored by TLC analysis (Silica Gel F-254 plates with toluene as developer). There appeared to be a gradual increase in **2** as the picryl chloride disappeared but at no time was there any evidence for a buildup of the intermediate (**1**).

The isolated yields of **2** from potassium dinitrotriazole, lithium dinitrotriazole, and a mixture containing potassium dinitrotriazole and 1 equiv of lithium chloride were 16, 20, and 28%, respectively. The increase in yield of **2** when lithium chloride is added to the reaction mixture would be expected since the increased chloride ion concentration would favor the reaction of **1** with chloride rather than nitrite ion. Presumably there was a decrease in the amount of **4** formed under these conditions but this was not established due to uncertainties in the yield of **4** (due to losses of **4** during the workup while attempting to separate it from picric acid and 3,5-dinitrotriazole).

Experimental Section

General. Caution! The compounds described herein are explosives and should be handled with care. Potassium and lithium dinitrotriazole were prepared by treating an ether–acetone solution of 3,5-dinitro-1,2,4-triazole[8] with the respective metal carbonates until the solution was slightly basic to wet litmus paper. The insoluble material was removed and washed well with acetone, and the dinitrotriazole salt was crystallized from the filtrate by concentration and addition of ether. The lithium salt after drying in a vacuum desiccator over phosphorus pentoxide retains appreciable water of hydration and melts with loss of water at ca. 120 °C, then slowly resolidifies and remelts at 315 °C dec. The potassium salt, after the same drying conditions, retains little or no water of hydration and has mp 223–225 °C. The IR spectra of the hydrated dinitrotriazole salts (K^+, Na^+, Li^+) show a large rather sharp peak near 3570–3600 cm^{-1} as well as two additional peaks between 3500 and 3200 cm^{-1}. A peak at 1645 cm^{-1} is also characteristic of the hydrates.

NMR spectra were determined on a Varian HA-100 spectrometer and the chemical shifts are relative to tetramethylsilane. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The melting points are uncorrected.

1-Picryl-3-nitro-5-chloro-1,2,4-triazole (2). Potassium dinitrotriazole (3.1 g, 0.157 mol) was dissolved in 25 mL of hot dry acetonitrile (dried by distillation from phosphorus pentoxide) and the solution was stirred with 3A molecular sieves for 20 h. Picryl chloride (3.1 g, 0.125 mol) was added and the mixture (protected by a phosphorus pentoxide–drierite drying tube) was stirred at gentle reflux for 46 h (Brown oxides of nitrogen were visible throughout the reaction). The cooled reaction mixture was filtered, the filtrate was poured into 200 mL of ice water, and the mixture was stirred for a short time until the precipitated oil turned to a semisolid. The aqueous solution was decanted from the semisolid which was then extracted into 50 mL of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and then quickly passed through a short column of silica gel 60 (ca. 1 in. long and $\frac{7}{8}$ in. in diameter contained in a 15-mL sintered glass funnel).

Concentration of the methylene chloride solution and addition of hexane gave 0.7 g (16%)[9] of cream-colored crystals, mp 158–160 °C. Recrystallization from methylene chloride raised the mp to 163–164 °C: NMR (CD_3COCD_3) δ 9.54 (s); mass spectrum *m/e* 359, 361 (M^+, chlorine isotopes).

Anal. Calcd for $C_8H_2N_7O_8Cl$: C, 26.71; H, 0.56; N, 27.27; Cl, 9.86. Found: C, 26.74; H, 0.68; N, 27.17; Cl, 10.01.

1-Picryl-3-nitro-1,2,4-triazol-5-one (4). The cooled reaction mixture from a run similar to that described above but starting with 10 g of picryl chloride was poured into 600 mL of ice water and the aqueous solution was decanted from the precipitated semisolid. The aqueous solution was first extracted with 150 mL of ether, strongly acidified with 30% sulfuric acid, and extracted a second time with 150 mL of ether. Removal of the solvent from the second ether extract gave a residue which was first extracted with 30 mL of 30% sulfuric acid and then with 40 mL of water at 60 °C.[10] The insoluble material (1 g, mainly **4** with some picric acid) was removed by filtration and then crystallized from acetone–water to give 0.45 g, mp 269–273 °C dec. Recrystallization from acetone/1,2-dichloroethane raised the mp to 276–278 °C dec: NMR (CD_3COCD_3) δ 9.24 (s, 2, aromatic H), 8.31 (broad s, 1, NH); mass spectrum *m/e* 341 (M^+); IR (KBr) 3335 (NH), 1760 (C=O) cm^{-1}.

Anal. Calcd for $C_8H_3N_7O_9$: C, 28.16; H, 0.89; N, 28.74. Found: C, 28.06; H, 0.90; N, 28.61.

Reaction of 1-Picryl-3-nitro-5-chloro-1,2,4-triazole (2) with Ammonia. A solution of 1.50 g of 1-picryl-3-nitro-5-chloro-1,2,4-triazole in 30 mL of methanol containing anhydrous ammonia gas was stirred at ambient temperature for 50 min. The precipitated crystals[11] (2,4,6-trinitroaniline) were removed by filtration and the solvent was allowed to evaporate from the filtrate. The residue was stirred with 5 mL of distilled water and the insoluble material (additional 2,4,6-trinitroaniline) was removed by filtration. The filtrate was first extracted with ether (to remove traces of trinitroaniline) before the water was allowed to evaporate to give crystals (0.62 g) of ammonium chloronitrotriazole, mp 170–174 °C dec. Crystallization from acetone–ether raised the mp to 173–175 °C dec.

Anal. Calcd for $C_2H_4ClN_5O_2$: C, 14.51; H, 2.44; N, 42.31; Cl, 21.42. Found: C, 14.43; H, 2.37; N, 42.58; Cl, 21.34.

Treatment of the ammonium chloronitrotriazole with dimethyl sulfate gave 1-methyl-3-nitro-5-chloro-1,2,4-triazole, mp 89–90 °C (lit.[6] mp 88–89 °C).

Acknowledgment. The author is grateful to R. N. Rogers and Mary Fowler of Los Alamos Scientific Laboratory for preliminary information regarding their procedure for the preparation of 3,5-dinitrotriazole.

Registry No.—**1**, 66652-93-5; **2**, 66652-94-6; **3**, 66652-95-7; **4**, 66652-96-8; **5**, 66652-97-9; 3,5-dinitro-1,2,4-triazole, 26621-32-9; 3,5-dinitro-1,2,4-triazolepotassium salt, 50738-33-5; 3,5-dinitro-1,2,4-triazolelithium salt, 66652-98-0; picryl chloride, 88-88-0; ammonium chloronitrotriazole, 66652-99-1; 1-methyl-3-nitro-5-chloro-1,2,4-triazole, 31123-18-9.

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(3) (a) A. A. Stotskii and N. P. Tkacheva, *Zh. Org. Khim.*, **10**, 2232 (1974); (b) A. A. Stotskii and N. P. Tkacheva, *ibid.*, **12**, 235 (1976).
(4) The only instance in the literature where N_4-alkylation of 3,5-dinitro-1,2,4-triazole has been suggested is for its reaction with nitroalkenes: D. V. Sickman, U.S. Patent 2 987 520 (June 6, 1961). Thus the reaction of 3,5-dinitrotriazole with nitroethylene was reported to give 4-(2-nitroethyl)-3,5-dinitro-1,2,4-triazole, mp 146–147 °C. However, this is open to dispute as later authors (ref 6) report this reaction to give 1-(β-nitroethyl)-3,5-dinitro-1,2,4-triazole, mp 146 °C. In general, N_4 substitution of 1,2,4-triazoles is extremely rare. The only other reported case of N_4 substitution is for alkylation of 5-furyl-3-amino-1,2,4-triazoles with methyl iodide in neutral media: E. Akerblom, *Acta Chem. Scand.*, **19**, 1142 (1965).
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(9) Lithium dinitrotriazole gave a 20% yield of product, mp 161–163 °C. Potassium dinitrotriazole with 1 equiv of lithium chloride gave a 28% yield of product, mp 162–164 °C.
(10) The 30% sulfuric acid extract removes mainly 3,5-dinitrotriazole after which the warm water extract removes mainly picric acid. Addition of concentrated hydrochloric acid to the warm water extract gave 0.5 g of picric acid.
(11) The crystals were shown to be 2,4,6-trinitroaniline by comparison (mp, UV, TLC) with an authentic sample.

Synthesis of Indole-2-carboxylic Esters

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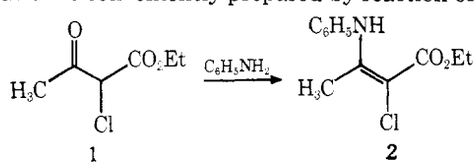
Recently, we reported that *N*-methyl-3-hydroxyindolines can be prepared in excellent yield by photocyclization–rearrangement of 2-(*N*-methylanilino)acetoacetates.[1] In acetic acid, the 3-hydroxyindolines undergo rapid dehydration to give *N*-methylindoles; alternatively, irradiation of the 2-(*N*-methylanilino)acetoacetate in acetic acid solution produces indoles directly. Experiments designed to probe the mechanism of 3-hydroxyindoline formation indicate that cyclization is completely stereoselective and occurs from the enol tautomer of the 2-anilinoacetoacetate.

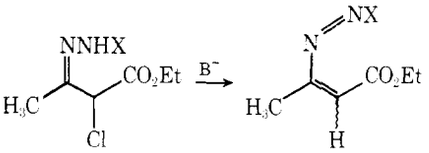
The 2-(*N*-methylanilino)acetoacetate required for indole preparation is conveniently prepared by reaction of the appropriate *N*-methylaniline with 2-chloro- or 2-bromoacetoacetate. However, reaction of aniline with ethyl 2-chloroacetoacetate (**1**) results in enamine formation to give **2** instead of the desired substitution product. Herein, we describe a useful, high yield preparation of *N*-unsubstituted-2-anilinoacetoacetates as well as their photoconversion to *N*-unsubstituted indoles.



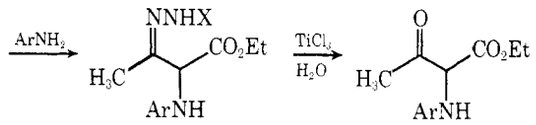
1 2

In 1960, Beyer and Badicke reported that the semicarbazone of ethyl 2-chloroacetoacetate **3a** undergoes base-catalyzed 1,4-elimination of hydrogen chloride to give azoene **4a** and that **4a** reacts in Michael fashion at C(2) with aniline to give the semicarbazone of ethyl 2-anilinoacetoacetate **5** in 65% yield.[2] We find the *N*-carbomethoxyhydrozone **3b** to be a superior intermediate;[3] azoene **4b** is produced by treatment of **3b** with mild base, and **4b** reacts with a variety of aniline derivatives to give addition products **6** in excellent yield (Table I).

Regeneration of the ketone carbonyl group in **6** is best accomplished by reaction with aqueous titanium trichloride,[4] from which the 2-anilinoacetoacetates **7** can be obtained

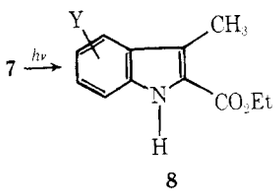


3a, X = $CONH_2$
b, X = CO_2CH_3 **4**



5, X = $CONH_2$; Ar = C_6H_5
6, X = CO_2CH_3 **7**

without the need for further purification. Pyrex-filtered irradiation of **7** in degassed benzene–methanol–acetic acid solution gives indoles **8** in excellent yield (Table I). We note that, except for example **7e**, alkoxy, halogen, and carbomethoxy



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substituents on the benzene ring are compatible with photocyclization. On the other hand, the *p*-nitro derivative **7i** failed to give an indole on extended irradiation. With meta-substituted anilines, cyclization results in both 6- and 4-substituted indoles; however, with *m*-bromo-2-anilinoacetate **7j**, cyclization occurs mainly away from the bromine atom to give a 6-bromoindole as the major reaction product by a factor of 10:1. A halogen atom can serve as a blocking group as illustrated with example **7n**, in which cyclization gives only the 4-methoxy-7-chloroindole. Eventual removal of halogen by hydrogenolysis or lithium aluminum hydride reduction would give the 4-methoxyindole with complete overall regioselectivity.

The methodology presented here represents the first report of N-unsubstituted indole preparation by photochemical means. We consider photocyclization of 2-anilinoacetoacetates to be a useful alternative to the traditional Bischler indole synthesis. Carbon–carbon bond formation occurs in the absence of strong acids, and, in contrast to the Bischler synthesis, electron deficient aniline derivatives give indoles in high yield. It should be noted that indole-2-carboxylic esters may be hydrolyzed and decarboxylated on treatment with copper chromite in quinoline.[5]