

and left for 96 hours. The colorless liquid obtained was decanted from the sticky matter, washed with water, and dried; the yield was 98% (29.6 grams). It was used directly for condensation.

INTERACTION OF BENZOYL AND *tert*-BUTYL ISOTHIOCYANATES WITH 2-AMINOBENZOTHAZOLES

Formation of *N*-Benzoyl-(or *tert*-Butyl)-*N'*-2-benzothiazolythioureas. Molar quantities of different 2-aminobenzothiazoles and benzoyl isothiocyanate and *tert*-butyl isothiocyanate reacted rapidly at room temperature in petroleum ether solution, giving high yields of *N*-benzoyl-(or *tert*-butyl)-*N'*-2-benzothiazolythioureas (Table I).

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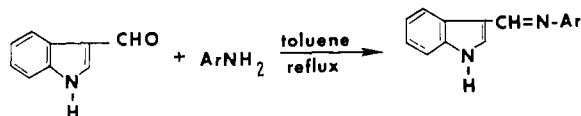
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3-(*N*-Substituted Formidoyl)indoles

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Several 3-(*N*-substituted formidoyl)indoles were synthesized and characterized. Yields, melting points, and elemental analyses are given for the reported compounds.

SEVERAL 3-(*N*-substituted formidoyl)indoles were synthesized and tested for biological activity. These compounds were prepared by refluxing a toluene solution of indole-3-carboxaldehyde and amine as described by a published procedure (1).



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Table I lists the yields, melting points, and elemental analyses of compounds prepared. Table II lists characteristic absorption bands for each compound. The infrared spectrum of each compound was consistent with the desired structure.

EXPERIMENTAL

Reactants were obtained commercially and used without further purification. Elemental analyses were performed by Carol K. Fitz, Needham Heights, Mass. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectro-

Table I. 3-(*N*-Substituted Formidoyl)indoles

No.	Compound	Ar	% Yield	Color	M.P., °C.	Empirical Formula	Analyses			
							% C	% H	% Cl	% N
1.	3-(<i>N</i> -phenyl formidoyl)indole		95	Pale yellow	127-128 ^a	C ₁₆ H ₁₂ N ₂	Calcd. 81.8 Found 81.8	5.5	...	12.7
2.	3-(<i>N</i> - <i>p</i> -fluorophenylformidoyl)indole		60	Pale green	142-144 ^b	C ₁₆ H ₁₁ FN ₂	Calcd. 75.6 Found 75.5	4.7	...	11.7
3.	3-(<i>N</i> - <i>p</i> -chlorophenylformidoyl)indole		95	Pale yellow	133-134 ^a	C ₁₆ H ₁₁ ClN ₂	Calcd. 70.7 Found 70.4	4.4	13.9	11.0
4.	3-(<i>N</i> -3,4-dichlorophenylformidoyl)indole		92	Pale yellow	176-178 ^c	C ₁₆ H ₁₀ Cl ₂ N ₂	Calcd. 62.3 Found 62.4	3.5	24.5	9.7
5.	2-(3-Indolylmethylene)-4-chloroanthranilic acid		95	Yellow	291-292 ^d	C ₁₈ H ₁₁ ClN ₂ O ₂	Calcd. 64.4 Found 64.2	3.7	11.9	9.4
6.	2-(3-Indolylmethylene)-5-chloroanthranilic acid		97	Green	310 (dec.)	C ₁₈ H ₁₁ ClN ₂ O ₂	Calcd. 64.4 Found 64.1	3.7	11.9	9.4
7.	3-(<i>N</i> - <i>m</i> -trifluoromethylphenylformidoyl)indole		95	Light green	158.5-159.5 ^b	C ₁₆ H ₁₁ F ₃ N ₂	Calcd. 66.7 Found 66.2	3.9	...	9.7
8.	3-(<i>N</i> -2-thiazoylformidoyl)indole		74	Orange	207 (dec.) ^b	C ₁₂ H ₉ N ₃ S	Calcd. 63.4 Found 63.1	4.0	...	18.5
9.	3-(<i>N</i> -2-pyridylformidoyl)indole		54	Orange	171-173 ^b	C ₁₄ H ₁₁ N ₃	Calcd. 75.9 Found 75.7	5.0

^a Recrystallized from benzene-ligroin. ^b Recrystallized from absolute ethanol. ^c Recrystallized from toluene. ^d Recrystallized from nitrobenzene.

Table II. Characteristic Infrared Absorption Bands of 3-(*N*-Substituted Formidoyl)indoles

No.	Aromatic C—H Stretch, Cm. ⁻¹	N—H Stretch, Cm. ⁻¹	Indole Ring Absorptions, Cm. ⁻¹	Aromatic C=C or C=N Stretch, Cm. ⁻¹	C—H Out-of-Plane Deformations, Cm. ⁻¹	Specific Absorptions, Cm. ⁻¹	No.	Aromatic C—H Stretch, Cm. ⁻¹	N—H Stretch, Cm. ⁻¹	Indole Ring Absorptions, Cm. ⁻¹	Aromatic C=C or C=N Stretch, Cm. ⁻¹	C—H Out-of-Plane Deformations, Cm. ⁻¹	Specific Absorptions, Cm. ⁻¹
1	3020	3120 2860	1248 1125	1610 1560 1480 1440 ^a	780 750 697	None	6	3030	2780 2600	1230 1140	1580 1450 1410 ^a	900 875 845 815 780 745	C—Cl 695 —CO ₂ ⁻ 1610 1350
2	3020	3080 2860	1240 1120	1613 1580 1493 1440 ^a	805 750	C—F 1190	7	3020	3080 2860	1244 1115	1610 1560 1480 1440 ^a	910 880 811 801 758	—CF ₃ 1190 1163 1328
3	3025	3330 3075 2850	1238 1115	1600 1560 1480 1430 ^a	831 755	C—Cl 705	8	3020	3080 2870	1240 1120	1600 1560 1480 1450 ^a	755	C—S— 725
4	3030	3120 2860	1245 1130	1610 1480 1570 1440 ^a	885 860 807 755	C—Cl 694	9	3010	3380 2810	1244 1120	1613 1594 1580 1555 1460 1430 ^a	740	
5	3020	2793 2604	1235 1120	1580 1460 1410 ^a	920 840 781 741	C—Cl 683 —CO ₂ ⁻ 1600 1350							

^a Band also in region for indole ring absorption.

photometer in a potassium bromide matrix. Melting points were taken on a Hershberg melting point apparatus and are uncorrected.

GENERAL PROCEDURE

A toluene solution of indole-3-carboxaldehyde (0.15 mole) and amine (0.15 mole) was refluxed until the required amount of water was collected in a Dean-Stark trap. The solvent was removed using a Büchler flash evaporator and the product was recrystallized as indicated in Table I.

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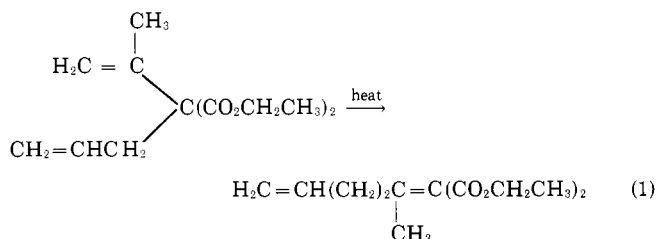
Solvent Effects in the Cope Rearrangement

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The rate of rearrangement of diethyl allylisopropenylmalonate has been measured in several solvents at 144.4° C. Several macroscopic solvent parameters for these solvents have also been evaluated at 144.4° C.

THE influence of the solvent on the rate of the concerted nonionic Cope rearrangement (1, 5, 9) of diethyl allylisopropenylmalonate (Equation 1) has been determined as part of our investigation (2, 3) of the role of the solvent in nonionic concerted reactions.



In Table I are presented the results obtained with non-hydrogen bonding solvents for the reaction in Equation 1 along with some solvent parameters evaluated at 144.4° C. Since the rate of the reaction is the same within experimental error in the solvents *n*-decane and anisole whereas the solvent parameters differ for these solvents, it is clear that none of these macroscopic parameters alone can adequately correlate the results.

Although solvent polarity would be expected to be a less important factor than nonelectrostatic solvent interactions in a nonionic concerted reaction, the dielectric constant function $(D - 1)/(2D + 1)$, evaluated at 144.4° C., has been included in Table I. Regular solution theory is applicable to systems in which dispersion forces (an example of nonelectrostatic interactions) predominate (6); the solubility