

cording to Lee-Kesler-Plöcker and Soave-Redlich-Kwong. The equation of state according to de Santis yields equilibrium compositions that differ from the other equations of state, which may be explained by the uncertainty in the temperature-dependent parameters determined from pressure-volume-temperature data at temperatures near the critical. All the equations of state studied yield results that differ from those obtained experimentally, when the differences in equilibrium composition between the vapor phase and the liquid phase are small.

Acknowledgment

The skillful assistance in the experimental work of Kaija Matikainen and of Lars-Göran Johannesson are gratefully acknowledged. We also acknowledge the valuable comments made by the reviewers.

Glossary

A, B	constants in the equation of state according to Redlich-Kwong and Soave-Redlich-Kwong
A, B, C, D	constants in the equation of state according to Lee-Kesler-Plöcker
P	pressure, Pa
T	temperature, K
v	mole volume, $\text{m}^3 \text{mol}^{-1}$
z	compressibility
R	gas constant per mole, $\text{J mol}^{-1} \text{K}^{-1}$
n	exponent in the equation of Lee-Kesler-Plöcker
k	interaction parameter
a, b	parameters in the equation of state according to Redlich-Kwong, Soave-Redlich-Kwong, and de Santis
a, b, c, d	constants in the equation of Lee-Kesler-Plöcker
x	mole fraction, liquid phase
y	mole fraction, vapor phase
z	mole fraction
f	fugacity
Greek Letters	
β	constant in the equation according to Lee-Kesler-Plöcker
γ	constant in the equation according to Lee-Kesler-Plöcker
ϕ	fugacity coefficient

Ω_a	constant in the equation according to Redlich-Kwong and Soave-Redlich-Kwong
Ω_b	constant in the equation according to Redlich-Kwong and Soave-Redlich-Kwong
ω	acentric factor

Superscripts and Subscripts

L	liquid phase
V	vapor phase
i, j	components
c	critical state
cm	pseudocritical state of a mixture
m	mixture
r	reduced state
(0)	simple fluid
(1)	function of deviation
(r)	reference fluid

Registry No. CCl_2F_2 , 75-71-8; $\text{C}_2\text{Cl}_2\text{F}_4$, 76-14-2; CHClF_2 , 75-45-6.

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Received for review October 19, 1988. Accepted January 24, 1989. We are indebted to the Swedish Building Research Council for financial support of the project.

NEW COMPOUNDS

Synthesis and Spectra of Some Phthalimido Derivatives

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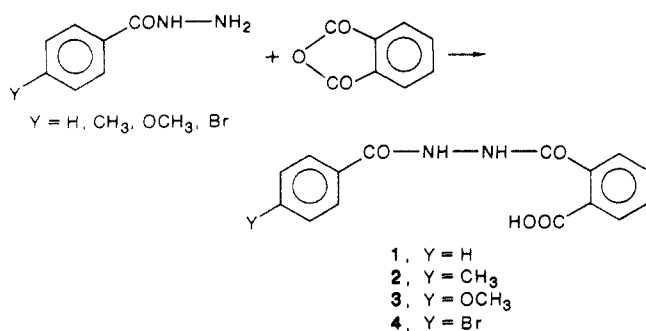
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The reactions of some aroylhydrazines and amino derivatives of heterocyclic compounds with phthalic anhydride were investigated. Dehydration of the prepared carboxybenzoyl derivatives afforded the corresponding phthalimido products. The structures were confirmed by IR, proton NMR, and mass spectra.

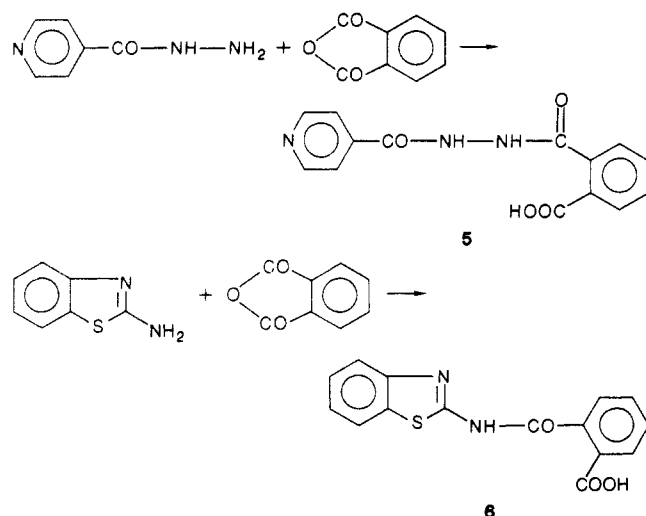
The phthaloyl group has an interesting feature in protection of amino sugars (1-3), amino acids (4), and peptides (5). Removal of the phthaloyl group by hydrazinolysis using hydrazine, phenylhydrazine, or methylhydrazine (6) is well-known. However, hydrazine remains the reagent of choice, because the deblocking can be performed under mild conditions.

1-Aroyl-2-(2'-carboxybenzoyl)hydrazines (1-4) were syn-

Scheme I



Scheme II



thesized by the reaction of the aroylhydrazines with phthalic anhydride in hot methanol to give quantitative yields (Scheme I).

The structures of these compounds were confirmed by their IR, NMR, and MS spectra as well as their elemental analyses.

In addition, phthalic anhydride reacted with isonicotinoylhydrazine and 2-aminothiazole to form products 5 and 6 (Scheme II).

The phthalimido derivatives (7–11) have been prepared in high yield (as shown in Scheme III) by dehydration of compounds 1–6 using a mixture of acetic anhydride and pyridine (1:1).

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. Infrared spectra were determined by use of KBr on a Unicam SP-1025 infrared spectrophotometer. ¹H NMR spectra were recorded on Varian EM 390, 90-MHz NMR spectrophotometer using tetramethylsilane as internal standard. Microanalyses were performed at the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt. The calculated and experimental values agreed and were submitted for review. The mass spectra were measured on Nuchik 12-90-G instrument.

Synthesis of 1-Aroyl-2-(2'-carboxybenzoyl)hydrazine (1–4). Aroylhydrazine (0.01 mol) was dissolved in methanol (50 mL) and phthalic anhydride (0.01 mol) added with stirring. The reaction mixture was refluxed for 3 h. After cooling at room temperature the product separated from the mixture. Filtration and crystallization from the appropriate solvent (Table I) afforded pure product.

Infrared spectra of compounds 1–4 are characterized by NH stretching at 3340–3210 cm⁻¹ and >C=O of the acid at 1740 cm⁻¹, while the amide >C=O appears at 1670 cm⁻¹.

Scheme III

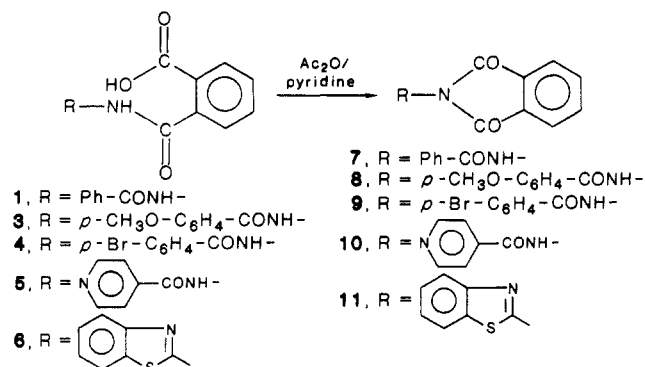


Table I. Mass Spectra, Melting Points, and Crystallization Solvent(s) of All Compounds

compd no.	mp, °C	S ^a	m/z (rel int)
1	150	E	284 (5), 136 (18), 122 (5), 105 (100), 77 (75)
2	235	E	268 (6), 148 (3), 120 (16), 119 (100), 91 (47), 67 (9)
3	249–259	E	296 (5), 136 (26), 135 (100), 107 (16), 104 (10), 92 (27), 77 (58)
4	268	E/C	344 (6), 344 (7), 214 (17), 183 (100), 166 (5), 155 (41), 122 (32), 105 (35), 104 (17)
5	187	E	267 (3), 166 (4), 162 (13), 137 (64), 106 (100), 105 (18), 104 (23), 79 (12), 78 (92), 76 (82)
6	191	E	249 (2), 123 (100), 106 (29), 78 (33)
7	218–220	E/W	266 (7), 106 (14), 105 (100), 77 (59)
8	160	P	296 (15), 149 (15), 147 (25), 135 (100), 107 (55), 92 (68), 77 (39)
9	207	M	346 (5), 183 (100), 155 (17), 104 (12), 76 (23)
10	220	E	267 (3), 162 (13), 137 (64), 122 (13), 107 (11), 106 (100), 105 (18), 104 (23), 79 (12), 78 (92), 77 (10)
11	143–147	E	280 (3), 192 (25), 105 (100), 123 (14), 96 (10)

^aSolvent(s) of crystallization: E, ethanol; C, chloroform; W, water; P, petroleum ether; M, methanol.

The ¹H NMR of compounds 1–4 (in CDCl₃) showed carboxylic protons at δ 10–11, and the N–H peak appeared as a singlet at δ 8.1–8.5. Both disappeared on addition of D₂O. The aromatic protons appeared as a multiplet at δ 7.3–7.8.

Synthesis of 1-Isonicotinoyl-2-(2'-carboxybenzoyl)hydrazine (5). Isonicotinoylhydrazine (0.01 mol) in methanol was treated with phthalic anhydride (0.01 mol) and worked up as before to give 1-isonicotinoyl-2-(2'-carboxybenzoyl)hydrazine (5). The IR spectra showed NH stretching at 3350 cm⁻¹ while the carbonyl of carboxylic acid appeared at 1730 cm⁻¹ and amide carbonyl stretching appeared at 1680 cm⁻¹. ¹H NMR spectrum (acetone-*d*₆) has two sets of doublets at δ 8.7 and 7.9, assigned to the pyridine protons, while the aromatic protons appeared as a multiplet at δ 7.3–8.0.

Synthesis of N-(2-Carboxybenzoyl)-2-aminothiazole (6). 2-Aminothiazole (0.01 mol) in methanol (40 mL) was treated with phthalic anhydride (0.01 mol), and the reaction proceeded as in the case of the aroylhydrazines (Table I).

The IR spectrum of N-(2'-carboxybenzoyl)-2-aminothiazole (6) has the NH stretching at 3350 cm⁻¹ and the carbonyl groups of acid and amide at 1740 and 1658 cm⁻¹, respectively. The aromatic signals in the ¹H NMR spectrum (acetone-*d*₆) appeared as a multiplet at δ 7.1–8.0.

Synthesis of the Phthalimido Derivatives (7–10). 1-Aroyl-2-(2'-carboxybenzoyl)hydrazine (0.01 mol) was added to acetic anhydride–pyridine mixture (50 mL, 1:1), and the reaction

mixture was stirred for 16 h at room temperature. Evaporation of the unreacted acetic anhydride-pyridine mixture under reduced pressure afforded the phthalimido product. Crystallization from the appropriate solvent (Table I) gave pure phthalimido compounds.

The IR spectra of compounds 7-10 showed NH stretching at 3350-3365 cm^{-1} and the amide carbonyl at 1680 cm^{-1} . The carbonyl groups of the carboxylic acids of compounds 7-11 disappeared, and a new band appeared at $\sim 1700 \text{ cm}^{-1}$ corresponding to the imido group ($-\text{CONH}-\text{CO}-$).

^1H NMR spectra of compounds 7-11 were in full agreement with these for compounds 1-6 except for the disappearance of the carboxylic and amide protons.

Registry No. 1, 16067-61-1; 2, 118071-17-3; 3, 118071-18-4; 4, 118071-19-5; 5, 70988-26-0; 6, 19357-13-2; 7, 16067-65-5; 8, 118071-20-8; 9, 118071-21-9; 10, 100873-73-2; 11, 60945-03-1; phthalic anhy-

dride, 85-44-9; benzoylhydrazine, 613-94-5; *p*-methylbenzoylhydrazine, 3619-22-5; *p*-methoxybenzoylhydrazine, 3290-99-1; *p*-bromobenzoylhydrazine, 5933-32-4; 4-pyridinecarboxylic acid hydrazide, 54-85-3; 2-aminobenzothiazole, 136-95-8.

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Received for review February 24, 1988. Revised June 8, 1988. Accepted October 31, 1988.

Regioselectivity of 1,3-Dipolar Cycloaddition Reactions of *C*-Acetyl-*N*-arylnitrilimines with Acrylic Acid Derivatives and α,β -Unsaturated Ketones

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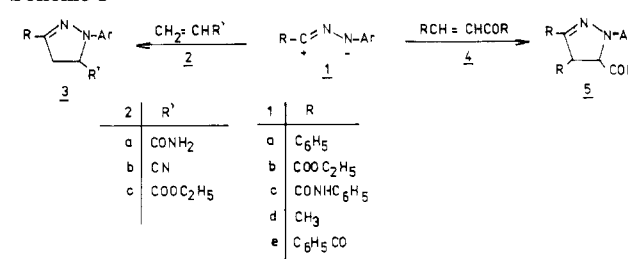
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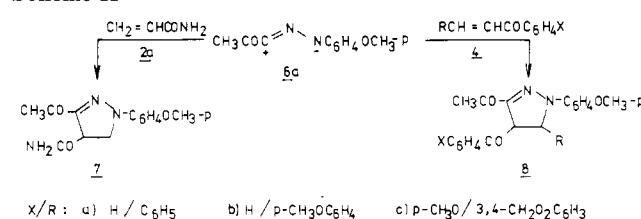
The cycloaddition of a series of *C*-acetyl-*N*-arylnitrilimines 6a-e to acrylamide (2a), acrylonitrile (2b), and substituted benzylideneacetophenones 4a-d has been studied. Under thermal conditions, these 1,3-dipolar cycloadditions proceed with absolute regioselectivity to yield 5-CONH₂-, 5-CN-, and 5-COAr-substituted 2-pyrazolines 3A, 3B, and 5, respectively. The structures of the cycloadducts 3A, 3B, and 5 were assigned on the basis of their ^1H NMR and IR spectra.

Nitrilimines 1a-e have been known to react with acrylic acid derivatives 2a-c to give predominantly 5-substituted 2-pyrazolines 3 (Scheme I) (1). Also, the reactions of 1a-c with benzylideneacetophenone (4; R = C₆H₅) have been reported to give predominantly 5-benzoyl-4-phenyl-2-pyrazolines 5 (Scheme I) (2, 3, 7). The regioselectivity of these reactions was satisfactorily rationalized in terms of the nitrilimine HOMO-dipolarophile LUMO interaction (2, 3). A recent report (4) indicated, however, that the reaction of *C*-acetyl-*N*-(*p*-methoxyphenyl)-nitrilimine (6a) with acrylamide (2a) and the substituted benzylideneacetophenones 4a-c gave exclusively 1-aryl-3-acetyl-5-aminocarbonyl-2-pyrazoline 7 and 1,5-diaryl-3-acetyl-4-aryl-2-pyrazolines 8a-c, respectively (Scheme II). The regiochemistry of such products is contrary to our expectation; therefore, we reexamined the regiochemistry of the cycloadditions of *C*-acetyl-*N*-arylnitrilimines 6a-e to acrylic acid derivatives and α,β -unsaturated ketones. In this article we report on the results of the study of the reactions of 6a-e with acrylamide (2a), acrylonitrile (2b), and a series of four substituted benzylideneacetophenones 4a-d (Scheme III).

Scheme I



Scheme II



Results and Discussion

The reactions of *C*-acetyl-*N*-arylnitrilimines 6a-e, generated in situ by treatment of *C*-acetyl-*N*-arylformohydrazidoyl chlorides 9a-e with triethylamine, with the dipolarophiles 2a, 2b, and 4a-d were carried out in refluxing chloroform. The results are summarized in Table I. These results indicate that the cycloadditions of 6 with acrylamide (2a), acrylonitrile (2b), and α,β -unsaturated ketones 4a-d are regioselective, yielding exclusively the corresponding 5-CONH₂, 5-CN, and 5-COC₆H₄R