Liberation of the base from an aqueous solution of the hydroiodide with ammonia gave crude IX melting at 218–222° (dec.). Recrystallization from ethanol to constant melting point provided prisms, m.p. 236–238° (dec.); λ_{max} 3.05, 3.25, 6.21, 6.45–6.52, 6.60, 6.74 μ; λ_{max} 234 mμ, ϵ_{max} 11,600, λ_{max} 262 mμ, ϵ 12,600 (literature[14] 232 and 264 mμ in methanol, ϵ_{max} 13,500).

Anal. Calcd. for $C_6H_{10}N_4S$: C, 42.33; H, 5.92; N, 32.91; S, 18.83. Found: C, 42.46; H, 5.80; N, 33.07; S, 18.71.

B. From ethylenethiourea and mercuric oxide. A suspension of 10 g. of yellow mercuric oxide and 5.0 g. of ethylenethiourea in 50 ml. of xylene was heated under reflux for 4 hr. and filtered hot. The dark insolubles were continuously extracted with chloroform and the combined xylene filtrate and chloroform extract was concentrated to dryness providing 1.21 g. of yellow solid, m.p. 155–190°. Two recrystallizations from ethanol resulted in 0.37 g. (9%) of IX, identified by mixed melting point [236–238° (dec.)] and infrared spectrum.

Conversion of IX *to* VI. A mixture of 3.00 g. of IX, 9.0 g. of yellow mercuric oxide, and 55 ml. of 50% ethanol was heated under reflux for 4.5 hr., was then filtered hot, and the dark insoluble part was washed thoroughly with hot ethanol. The combined solution was concentrated to dryness and the gummy residue (1.15 g.) was dissolved in acetone and the solution was filtered. Concentration to low volume provided 0.14 g. (5%), m.p. 188–202°, which after recrystallization from acetone-benzene amounted to 0.11 g. of VI, m.p. and mixed m.p. 200–204° (dec.), further identified by infrared spectrum.

O-Methylation of ethyleneurea. A mixture of 8.6 g. (0.10 mole) of ethyleneurea and 18.6 g. (0.10 mole) of methyl *p*-toluenesulfonate was heated at 100° for 4 hr. by the method of Behringer and Meier.[8] The cooled mixture was distributed between ether and dilute hydrochloric acid and the acid layer was made basic and extracted with ether. From the dried ether extract there was obtained a small amount of oily solid which gave an infrared spectrum very similar to that of 2-methoxy-2-imidazoline (II). A picrate was obtained from methanol, which after one recrystallization amounted to 0.50 g. (1.5%) of II-picrate, m.p. 164–166°, identified by mixed melting point and infrared spectrum.

1-Methyl-2-imidazolinone. The procedure known to *O*-methylate caprolactam[5] was applied to ethyleneurea. In this case, a heterogeneous reaction mixture was obtained. From 17.2 g. (0.2 mole) of ethyleneurea and 25.2 g. (0.2 mole) of dimethylsulfate, there was obtained 15.9 g. of organic material after work-up. Fractional crystallization from ethyl acetate provided 2.8 g. (16%) of unchanged starting material, identified by melting point (128–131°) and infrared spectrum. The remainder was chromatographed over alumina. No 2-methoxy-2-imidazoline could be detected. The first material to be eluted (with mixtures of ether–petroleum ether and with ether) was crystalline 1-methyl-2-imidazolinone, melting first at 100–110° and then at 110–112° in later fractions. Purification by recrystallization from benzene and benzene-ether gave 2.3 g. (11%), m.p. 115–116°; λ_{max} 3.07, 3.22, 5.95, 6.60 μ.

Anal. Calcd. for $C_4H_8N_2O$: C, 47.98; H, 8.05; N, 27.98. Found: C, 48.14; H, 7.93; N, 27.60.

Heating ethyleneurea with methylsulfate by the method used to make methylisourea[6] gave very similar results.

PHILADELPHIA 32, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

1,3-Disubstituted Indeno[1,2-*c*]pyrazol-4-ones[1]

ROBERT A. BRAUN AND WILLIAM A. MOSHER[2]

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The reaction of hydrazine with 2-pivalyl, 2-benzoyl, and 2-*p*-methoxy-1,3-indandiones give the corresponding 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones in good yields. These compounds give *N*-sodium and potassium salts which react readily with active halogen compounds to give a new class of fluorescent compounds, 1,3-disubstituted indeno[1,2-*c*]pyrazol-4-ones. The infrared absorption spectra are discussed.

In connection with our earlier work on the Wolff-Kishner reduction of 2-acyl-1,3-indandiones,[3] we showed that 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones were intermediates in the reduction. The primary purpose of the investigation reported here was to study 3-substituted-indeno[1,2-*c*]-pyrazol-4(1*H*)-ones and their reactions, with emphasis on the new compounds, 1,3-disubstituted indeno[1,2-*c*]pyrazol-4-ones.

The cyclization of β-diketones with hydrazine to give pyrazoles has been studied extensively,[4] but prior to our work there has been no report of the cyclization reaction of 2-acyl(aroyl)-1,3-indandiones with hydrazine. A somewhat related reaction was studied by Ruhemann[5] and later by Leucks and Kowalski.[6] They found that ethyl-1-hydrindone-2-oxalate reacted with phenyl hydrazine to give ethyl-1-phenylindeno[1,2-*c*]pyrazole-3-carboxylate.

In our study of the monohydrazones of 2-acyl-(aroyl)-1,3-indandiones we observed that certain indandiones did not give monohydrazones, but cyclized very rapidly. 2-Pivalyl, 2-benzoyl, or 2-*p*-methoxybenzoyl-1,3-indandione reacts with one equivalent of hydrazine in refluxing alcohol to give white crystalline compounds resulting from the elimination of two moles of water, as shown by elemental analyses and molecular weight de-

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(1) From the dissertation submitted by Robert A. Braun in partial fulfillment of the requirements for the Ph.D. degree, University of Delaware.

(2) To whom inquiries should be addressed.

(3) R. A. Braun and W. A. Mosher, *J. Am. Chem. Soc.*, **80**, 4919 (1958).

(4) H. Gilman, *Organic Chemistry, An Advanced Treatise*, John Wiley & Sons, Inc., New York, N. Y., 1953, Vol. IV, p. 774.

(5) S. Ruhemann, *J. Chem. Soc.*, **101**, 1731 (1912).

(6) H. Leucks and G. Kowalski, *Ber.*, **58B**, 2288 (1958).

TABLE I

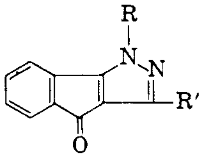
3-SUBSTITUTED INDENO[1,2-*c*]PYRAZOL-4(1*H*)-ONES (II)

				Analyses, %					
				Carbon		Hydrogen		Nitrogen	
R	Yield, %	M.P., °C.[a]	Empirical Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C(CH_3)_3$	99.0[b]	191–192[d]	$C_{14}H_{14}N_2O$	75.31	75.02	6.18	6.27	12.40	12.38
C_6H_5	98.3[c]	254–255[e]	$C_{16}H_{10}N_2O$	78.04	77.84	4.09	4.10	11.36	11.48
p-$CH_3OC_6H_5$	84.8[b]	264–265[f]	$C_{17}H_{12}N_2O_2$	73.90	74.19	4.38	4.68	10.14	10.23

[a] All melting points are corrected. [b] Reaction time, 2 hr. [c] Reaction time, 24 hr. [d] Recrystallized from aqueous methanol. [e] Recrystallized from ethanol. [f] Recrystallized from methanol-dimethylformamide.

TABLE II

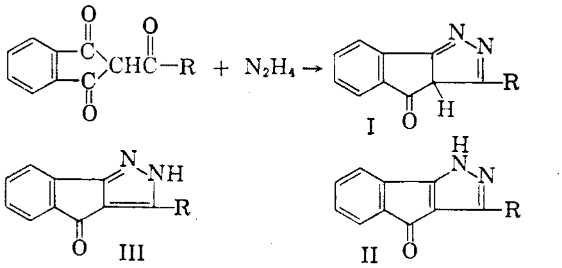
1,3-DISUBSTITUTED INDENO[1,2-*c*]PYRAZOL-4(1*H*)-ONES



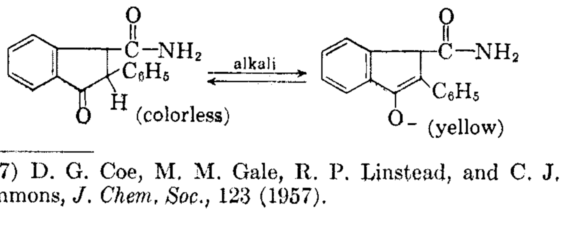
R	R′	Empirical Formula	Yield, %	M.P., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
C_2H_5	p-$OCH_3C_6H_4$	$C_{19}H_{16}N_2O_2$	80.2	156–156.5	9.20	9.34[a]
C_2H_5	C_6H_5	$C_{18}H_{14}N_2O$	88.4	140.5–141	10.21	9.96
C_6H_5CO—	$C(CH_3)_3$	$C_{21}H_{18}N_2O_2$	92.3	101–102	8.48	8.43[b]
C_2H_5COO—	$C(CH_3)_3$	$C_{17}H_{18}N_2O_3$	78.0	147.5–148.5	9.39	9.24[c]
C_2H_5COO—	C_6H_5	$C_{19}H_{14}N_2O_3$	97.0	163–164	8.80	8.78
C_2H_5COO—	p-$OCH_3C_6H_4$	$C_{20}H_{16}N_2O_4$	97.4	174.5–175	8.04	7.83
$C_6H_5SO_2$—	p-$OCH_3C_6H_4$	$C_{23}H_{16}N_2O_4S$	81.9	224.5–225.5	6.73	6.71

[a] Carbon, calcd. 74.98, found 74.94. Hydrogen, Calcd. 5.30, found. 5.23. [b] Carbon, calcd. 76.34, found 76.35. Hydrogen, Calcd. 5.49, found 5.41. [c] Carbon, calcd. 68.44, found 68.55.

termination. Their infrared spectra showed strong carbonyl bands and they also formed 2,4-dinitrophenylhydrazones. From the above information it is evident that structures I–III must be considered.



Upon initial examination it was thought that I was the correct structure since these compounds reacted with base in the same way as IV which was studied by Coe *et al.*[7] Structure I, however, is not consistent with the infrared spectra of these compounds as each has a band in the 3.1μ region, due to a hydrogen bonded N—H group.[3] The correct structure (II) has been distinguished from the alternate structure (III) by spectral evidence. The proof of this type of structure has been presented in a previous paper.[3] The properties and analyses of the 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones are summarized in Table I.



The 3-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-

TABLE III

PRINCIPAL INFRARED ABSORPTION BANDS (μ)[a] OF 1,3-DISUBSTITUTED (INDENO[1,2-*c*]PYRAZOL-4(1*H*)-ONES)

R	R′	C═O	N—H (Hydrogen Bonded)	(C═N, C═C)
H	$C(CH_3)_3$	5.88	3.4[b]	6.19
H	C_6H_5	5.96	3.4[b]	6.21
H	p-$OCH_3C_6H_4$	5.96	3.3[b]	6.21
C_2H_5	p-$OCH_3C_6H_4$	5.93	..	6.20
$COOC_2H_5$	$C(CH_3)_3$	5.67[c] 5.87[d]	..	6.20
$COOC_2H_5$	C_6H_5	5.72[c] 5.91[d]	..	6.23
$COOC_2H_5$	p-$OCH_3C_6H_4$	5.67[c] 5.87[d]	..	6.18
COC_6H_5	$C(CH_3)_3$	5.98[e] 5.90[d]	..	6.29

[a] Infrared recording spectrophotometer, Model B, Baird Associates, Inc., Cambridge, Mass. [b] Very wide and intense band. [c] Ester carbonyl. [d] Carbonyl on indan ring. [e] Amide carbonyl.

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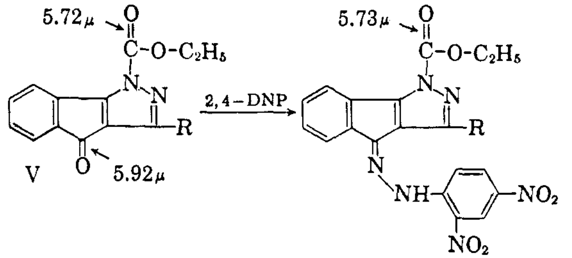
(7) D. G. Coe, M. M. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.*, 123 (1957).

ones reacted with hot alcoholic potassium hydroxide or hot aqueous sodium hydroxide to give insoluble yellow salts that were stable at room temperature although they could not be purified by recrystallization from water, alcohol, or dimethylformamide-ethanol. These were shown, by reaction with a series of active halogen compounds (ethyl bromide, ethyl chloroformate, benzoyl chloride, and benzenesulfonyl chloride), to be the *N*-alkali salts. Analytical data for these new compounds are shown in Table II and their spectral properties are summarized in Table III.

To establish further the carbonyl band assignment, the 2,4-dinitrophenylhydrazone of V was prepared and its spectrum shows only one carbonyl band at 5.73μ, because of the ester carbonyl.



R = *p* – $OCH_3C_6H_4$

All of the *N*-substituted indeno[1,2-*c*]pyrazol-4-(1*H*)-ones were yellow crystalline solids and were extremely fluorescent under ultraviolet light both in the solid state and in solution. This finding was unexpected as the parent 3-substituted indeno-[1,2-*c*]pyrazol-4(1*H*)-ones were not fluorescent. Although the 1,3-disubstituted indeno [1,2-*c*]-pyrazol-4(1*H*)-ones are similar in some respects to the fluorescent benzo-bispyrazolones,[8] they represent a new class of fluorescent compounds.

EXPERIMENTAL[9]

3-t-Butylindeno[1,2-c]pyrazol-4(1H)-one. Experimental details for the preparation of this compound from 2-pivalyl-1,3-indandione and hydrazine were given in an earlier paper.[3] The properties of the other 3-substituted indeno[1,2-*c*]-pyrazol-4(1*H*)-ones are shown in Table I. A yield of 99.0% of 3-*t*-butylindeno[1,2-*c*]pyrazol-4(1H)-one was obtained by using anhydrous ethanol as solvent and 95% pure hydrazine, while a 50% yield of the same product was obtained by running the reaction at 25° for 2 hr. The two other compounds of this type were prepared in the same way and their properties are summarized in Table I.

Sodium salt of 3-t-butylindeno[1,2-c]pyrazol-4(1H)-one. 3-*t*-Butylindeno[1,2-*c*]pyrazol-4(1*H*)-one (1.58 g., 0.007 mole) was mixed at room temperature with 50 ml. of 10% aqueous sodium hydroxide, but the white solid did not dissolve. After warming at 80° for 3 min. a clear yellow solution was obtained which was filtered through a fritted glass filter. The filtrate crystallized upon cooling. The yellow needles were collected and dried at 100°; yield, 1.70 g. (97.7%). Its melting point was greater than 350°. All attempts at recrystallization were unsuccessful.

High yields of the potassium salts could be obtained using hot alcoholic potassium hydroxide. The sodium and potassium salts of 3-phenyl- and 3-*p*-methoxyphenylindeno-[1,2-*c*]pyrazol-4(1*H*)-one are yellow high melting solids.

1-Ethyl-3-p-methoxyphenylindeno[1,2-c]pyrazol-4-one. A mixture of 1.00 g. (0.0033 mole) of the sodium salt of 3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one and a large excess (5 ml.) of ethyl bromide in 20 ml. of ethanol was refluxed for 5 hr. The solvent and excess ethyl bromide were evaporated and the residue was dried at 70°. After recrystallization from methanol the yellow fluorescent crystals of 1-ethyl-3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-4-one melted at 156–156.5°.

Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.94; H, 5.230 N, 9.34.

1-Benzenesulfonyl-3-methoxyphenylindeno[1,2-c]pyrazol-4-one. Benzenesulfonyl chloride (0.7 g., 0.004 mole) was added to a slurry of 1.00 g. (0.0033 mole) of the sodium salt of 3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one in 30 ml. of ether and the mixture was warmed at reflux for 30 min. The resulting solid was filtered, washed with ether, and recrystallized from a mixture of dimethylformamide and ethanol to give strongly fluorescent, light yellow needles, m.p. 224.5–225.5°.

Anal. Calcd. for $C_{23}H_{16}N_2O_4S$: N, 6.73. Found: N, 6.71.

Ethyl 4-oxo-3-p-methoxyphenylindeno[1,2-c]pyrazol-1-carboxylate. Ethyl chloroformate (0.38 g., 0.0035 mole) was added to a slurry of the sodium salt of 3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-4(1*H*)one (1.00 g., 0.0033 mole) in 20 ml. of ether. There was an immediate exothermic reaction and the color changed from a nonfluorescent pale yellow to a bright, strongly fluorescent yellow color. After refluxing for 10 min. the solid was collected and washed with ether, yielding 1.12 g. (97.4%) ethyl 4-oxo-3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-1-carboxylate; m.p. 173–175.° After recrystallization from dimethylformamide-methanol the compound melted at 174.5–175°. This material fluoresced intensely with a yellow-green color under ultraviolet light.

Anal. Calcd. for $C_{20}H_{16}N_2O_4$: N, 8.04. Found: N, 7.83.

The same procedure was used to prepare the other compounds of this type. Their properties are summarized in Table II.

These compounds can also be prepared by the reaction of excess ethyl chloroformate with 3-substituted indeno(1,2-*c*)-pyrazol-4(1*H*)-ones but the yields are much lower (5 to 20%).

The *2,4-dinitrophenylhydrazone* of ethyl 4-oxo-3-*p*-methoxyphenylindeno[1,2-*c*]pyrazol-1-carboxylate was recrystallized from ethyl acetate, m.p. 237–238°. The orange needles are not fluorescent. The infrared spectrum contains a N—H band at 3.05μ and a strong ester carbonyl band at 5.73μ.

1-Benzoyl-3-butylindeno[1,2-c]pyrazol-4-one. A 0.50 g. (0.002 mole) sample of the sodium salt of 3-*t*-butylindeno-[1,2-*c*]pyrazol-4(1*H*)-one was suspended in 10 ml. of anhydrous ether and excess (0.8 ml.) benzoyl chloride was added at room temperature. After warming in a hot water bath for 10 min. the yellow solid was filtered, dried, and crystallized from ethanol to give strongly fluorescent, yellow needles; yield, 0.52 g. (92.3%); m.p. 101–102°.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found; C, 76.35; H, 5.41; N, 8.43.

NEWARK, DEL.

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[8] S. Veibel and H. Lillelund, *Tetrahedron*, 1, 201 (1957).

[9] Microanalyses by the Geller Microanalytical Laboratories, West Englewood, N. J. All melting points are corrected.