ture to give 5 g. (23%) of a yellow compound melting at 124–125°.

Anal. Calcd. for $C_{22}H_{20}N_2$: N, 8.97. Found: N, 8.86.

2-[*p*-(2,5-Dimethylpyrryl-1)-phenyl]-quinoline.—From *p*-(2,5-dimethylpyrryl-1)-phenyllithium and quinoline, by procedures like those described in the preceding preparation, was obtained a 5% yield of compound melting at 149–150° after crystallization from ethanol. The nitrobenzene oxidation of the dihydro compound was a little troublesome in this preparation. The 2-[*p*-(2,5-dimethylpyrryl-1)-phenyl]-quinoline was shown to be identical (mixed melting point) with the compound obtained earlier[7] by condensation of 2-(*p*-aminophenyl)-quinoline with acetonylacetone.

Anal. Calcd. for $C_{21}H_{18}N_2$: N, 9.51. Found: N, 9.53.

The picrate after crystallization from ethanol melted at 176–177°.

Anal. Calcd. for $C_{27}H_{21}O_7N_5$: N, 13.2. Found: N, 13.2.

2-[*p*-(2,5-Dimethylpyrryl-1)-phenyl]-pyridine.—From *p*-(2,5-dimethylpyrryl-1)-phenyllithium and pyridine (8 g.) was obtained (subsequent to dry air oxidation of the dihydro compound) 6 g. (24.2%) of compound distilling at 170–172° (2 mm.) and melting at 93–94° after recrystallization from petroleum ether (b. p., 77–115°).

Anal. Calcd. for $C_{17}H_{16}N_2$: N, 11.29. Found: N, 11.22.

9-Substituted-2-methoxy-6-chloroacridines.—The condensations of pyrrole, 2,5-dimethylpyrrole, and piperidine with 2-methoxy-6,9-dichloroacridine were carried out in essential accordance with the procedure of Mueller and Hamilton.[8] In each case, 8.3 g. (0.03 mole) of 2-methoxy-6,9-dichloroacridine was heated with 10 cc. of the amine for four hours at 140°. The mixture, which solidified on cooling, was transferred to a suction filter to remove the excess of amine, and the product was recrystallized from 95% ethanol.

In these condensations, there was more resinification with 2,5-dimethylpyrrole than with pyrrole; and more with pyrrole than with piperidine. The solubilities in 95% ethanol were in the reverse order: 2,5-dimethylpyrryl- >pyrryl- >piperidyl.

The results are contained in Table II, and the additional related preparation which follows the table.

TABLE II

9-SUBSTITUTED-2-METHOXY-6-CHLOROACRIDINES

Product, 2-methoxy-6-chloro-9-	M. p., °C.	Yield, %	N, %	
			Calcd.	Found
-(1-pyrryl)acridine	245–246	65	9.07	9.20
(2,5-dimethylpyrryl-1)-acridine	225–226	40	8.32	8.16
-(1-piperidyl)acridine	136–137	85	8.57	8.73

2-Methoxy-6-chloro-9-[γ-(2,5-dimethylpyrryl-1)-propylamino]-acridine.—A mixture of 8.34 g. (0.03 mole) of 2-methoxy-6,9-dichloroacridine, 5 g. of phenol, and 5 cc. of 1-(γ-aminopropyl)-2,5-dimethylpyrrole was heated at 130° for eight hours. The solid obtained on cooling was washed with 10% sodium hydroxide to remove the phenol, and the residue was recrystallized from a benzene–petroleum ether mixture to give 4 g. (34%) of product melting at 185–186°.

Anal. Calcd. for $C_{23}H_{24}ON_3Cl$: N, 10.66. Found: N, 10.47.

Acknowledgment.—The authors are grateful to Drs. R. J. Porter and L. T. Coggeshall of the University of Michigan, for the antimalarial tests, the results of which will be published elsewhere.

Summary

A series of pyrryl derivatives of pyridine, quinoline and acridine has been made by reactions involving: (1) condensation of amines with acetonylacetone; (2) condensation of reactive chlorine with pyrrole and 2,5-dimethylpyrrole; (3) addition of RLi compound containing a basic group to pyridines and quinolines having the 2,5-dimethylpyrryl group as a substituent; and (4) addition of *p*-(2,5-dimethylpyrryl)-phenyllithium to the anil linkage of pyridines and quinolines.

AMES, IOWA RECEIVED[9] FEBRUARY 17, 1944

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(7) Unpublished studies by S. M. Spatz.

(8) Mueller and Hamilton, THIS JOURNAL, **65**, 1017 (1943).

(9) This manuscript was originally received on February 17, 1944 and after examination by the Editorial Board was accepted for publication in the Journal. It was, however, referred to the National Defense Research Committee and at their request was withheld from publication, in a confidential file, until clearance was granted on October 8, 1945.—*The Editor.*

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF GEORGIA]

The Synthesis of Several Dinitrodiphenylthiocarbazides and a Dinitrodiphenylthiocarbazone

BY ALFRED W. SCOTT AND C. R. SPELL[1]

Diphenylthiocarbazide and diphenylthiocarbazone have been found to give precipitates or color reactions with aqueous solutions of seventeen and nine inorganic cations, respectively.[2] The introduction of a nitro group, especially in the para position, into 1-allyl-4-phenyl thiosemicarbazide[3] has been found to increase the sensitivity of this reagent in the detection of silver and of mercury.

The purpose of this investigation was to prepare several isomeric dinitrodiphenylthiocarbazides and a dinitrodiphenylthiocarbazone, and to observe the influence of the position of the nitro groups upon the sensitivity of the reagents.

Distilled water solutions (1 g./liter) of the C. P. metallic nitrates of most of the cations usually

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(1) Constructed from a thesis by C. R. Spell, presented to the Graduate Faculty of the University of Georgia, in partial fulfillment of the requirements for the degree of Master of Science.

(2) "Tables of Reagents for Inorganic Analysis," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1938; Ibert Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Co., Philadelphia, 1941; K. Heller and P. Krumholz, *Mikrochemie*, **8**, 33 (1930); P. Krumholz and F. Hönel, *Mikrochim. Acta*, **3**, 306 (1936); John H. Yoe and L. A. Sarver, "Organic Analytical Reagents," John Wiley and Sons, New York, 1941.

(3) Alfred W. Scott and J. T. Andrews, THIS JOURNAL, **64**, 2873 (1942).

encountered in elementary schemes of qualitative analyses were tested. In the cases where very good reactions occurred, dilutions of the original solutions were made to determine sensitivities. Nitro groups in the ortho or para position were found to give the best results. Of these new compounds, the 4,4′-dinitrodiphenylthiocarbazone gave the best results but, except for mercury, its sensitivity was considerably less than those listed for "dithizone".[2] Dithizone is listed as being sensitive for mercury at 0.005 g./liter, while we found the 4,4′-dinitro derivative to give a red precipitate at 0.01 g./liter, and a pink solution at 0.001 g./liter.

Experimental

Nitrogen determinations were made by the Dumas method and sulfur determinations by the sodium peroxide method, using a Parr bomb.

3,3′-Dinitrodiphenylthiocarbazide.—*m*-Nitrophenylhydrazine was obtained from a saturated aqueous solution of the hydrochloride by the addition of sodium acetate and recrystallization from benzene. An attempt to prepare 3,3′-dinitrodiphenylthiocarbazide by the method used for the synthesis of diphenylthiocarbazide by Parri[4] proved unsuccessful. Apparently, the nitrophenylhydrazine dissolved very slightly in the carbon disulfide and even after six hours of refluxing, no evidence of the evolution of hydrogen sulfide was observed. The following method gave a 26% yield. Two grams of *m*-nitrophenylhydrazine and 10 ml. of C. P. carbon disulfide were dissolved in 50 ml. of 95% ethanol and refluxed. After fifteen minutes hydrogen sulfide was detected at the top of the condenser with moist lead acetate paper. After forty-five minutes, small lemon-yellow crystals were visible in the reaction mixture which began to darken slightly in color. After six hours the evolution of hydrogen sulfide ceased, the mixture was permitted to cool, and the solid filtered off. Several recrystallizations from alcohol gave powdery lemon-yellow crystals, melting at 169–171° (uncor.) with decomposition. It was soluble in acetone, slightly soluble in alcohol and insoluble in benzene, ether and ligroin.

Anal. Calcd. for $C_{13}H_{12}O_4N_6S$: N, 24.13; S, 9.2. Found: N, 23.89; S, 9.19.

This compound was found to cause precipitation of mercurous and mercuric mercury and cupric copper at concentrations of 1 g./liter.

2,2′-Dinitrodiphenylthiocarbazide was made in the same manner as the 3,3′-compound described above. The *o*-nitrophenylhydrazine used in this preparation was made from *o*-nitroaniline by the procedure outlined by Bischler.[5] Recrystallization from alcohol gave orange-red rhombic crystals melting at 195–197° (uncor.) with decomposition. The yield was 45% of the theoretical. The compound is fairly soluble in acetone, slightly soluble in alcohol and insoluble in ether, benzene, chloroform, carbon tetrachloride and petroleum ether.

Anal. Calcd. for $C_{13}H_{12}O_4N_6S$: N, 24.13; S, 9.2. Found: N, 24.41; S, 9.26.

4,4′-Dinitrodiphenylthiocarbazide was made in the same manner as the 3,3′-compound except that after refluxing for two hours only a slight amount of hydrogen sulfide was being evolved. After six hours hydrogen sulfide was being evolved freely but no solid was observed in the reaction mixture. Refluxing was continued intermittently for forty-eight hours over a four-day period, at the end of which time an orange-red solid was filtered off, washed with cold alcohol, dried in a vacuum and weighed. The yield of the crude product which melted at about 210–212° was a little less than 50% of the theoretical. Repeated recrystallizations from 50% aqueous alcohol gave dark brown needles melting at 205° (uncor.). The change in color and lowering of the melting point seemed to indicate the possibility of it being a decomposition product rather than the desired compound. It was later shown to be 4,4′-dinitrodiphenylthiocarbazone described later in this paper. The use of methanol, *n*-propanol and *n*-butanol as recrystallization solvents all gave the same result. Finally, the crude orange-red solid was recrystallized from nitrobenzene in the form of fine powdery orange-yellow crystals melting at 213–215° (uncor.) with decomposition. Only 25% of the purified product was obtained from the crude material after recrystallization. The orange-yellow crystals were very soluble in acetone, slightly soluble in water and in alcohol, and were insoluble in benzene, chloroform, petroleum ether and carbon tetrachloride.

Anal. Calcd. for $C_{13}H_{12}O_4N_6S$: N, 24.13; S, 9.2. Found: N, 23.92; S, 9.0.

4,4′-Dinitrodiphenylthiocarbazone was made by boiling 1 g. of 4,4′-dinitrodiphenylthiocarbazide for ten minutes in 50 ml. of alcoholic potash. The solution was neutralized with sulfuric acid and filtered. The product was recrystallized from 50% aqueous alcohol and gave dark brown needles melting at 205° (uncor.) with decomposition. A similar method was employed by Fischer[6] to convert diphenylthiocarbazide into the corresponding diphenylthiocarbazone. A mixed melting point with the brown compound prepared under 4,4′-dinitrodiphenylthiocarbazide also melted at 205°. It was very soluble in acetone, slightly soluble in alcohol and water, and insoluble in benzene, ether, chloroform, petroleum ether and carbon tetrachloride.

Anal. Calcd. for $C_{13}H_{10}O_4N_6S$: N, 24.27; S, 9.24. Found: N, 24.04; S, 9.14.

Qualitative tests were run on ions at concentrations of 10 g. per liter and dilutions thereof, using about six drops of the organic reagent to four ml. of the cation solution. None of the reagents was very soluble in water, the carbazone being the most soluble. In all cases, the organic reagent used was prepared by dissolving one-tenth gram of the organic compound in 100 ml. of acetone. Six to eight drops of the acetone reagent, when added to four ml. of water, would not cause a precipitation of the organic compound except in the case of the 2,2′-dinitrodiphenylthiocarbazide which would precipitate on long standing. The analytical results listed were found to be obtained from dilute acid solutions as well as from neutral solutions.

TABLE I

CONCENTRATIONS AT WHICH PRECIPITATES OR COLORED SOLUTION(S) ARE FORMED BY ISOMERIC DINITRODIPHENYLTHIOCARBAZIDES AND BY 4,4′-DINITRODIPHENYLTHIOCARBAZONE

	Grams/liter = 1:1000			
	Cu^{++}	Hg^{+}	Hg^{++}	Ag^{+}
3,3′-Azide	1 (b-s)	1 (p-s)	1 (p-s)	...
2,2′-Azide	0.01 (b)	0.1 (o-r)	0.1 (o-r)	0.1 (r-b)
4,4′-Azide	0.001 (b)	0.1 (o-r-s)	0.01 (r)	0.1 (g)
4,4′-Azone	0.01 (b)	0.001 (p-s)[a]	0.01 (r)	0.1 (g)

[a] = red precipitate at 0.01 g./l., b = brown, o = orange, g = green, p = pink, r = red, s = colored solution.

Summary

1. The following compounds were synthesized: 2,2′-dinitrodiphenylthiocarbazide, 3,3′-dinitrodiphenylthiocarbazide, 4,4′-dinitrodiphenylthiocarbazide and 4,4′-dinitrodiphenylthiocarbazone.

2. The isomers with nitro groups in the para position in diphenylthiocarbazide showed the greatest sensitivity in the detection of three cat-

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[4] W. Parri, *Giorn. farm. chim.*, **73**, 207 (1924), through *C. A.*, **19**, 223 (1925).

[5] Bischler, *Ber.*, **22**, 2801 (1889).

[6] E. Fischer, *Ann.*, **190**, 120 (1878).

ions, whereas those with meta nitro groups were least sensitive.

3. 4,4′-Dinitrodiphenylthiocarbazone may be used to advantage for a test for mercurous mercury in concentrations as great as 1/1,000,000.

ATHENS, GA. RECEIVED[7] OCTOBER 29, 1945

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[7] Original manuscript received November 24, 1944.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, PHILADELPHIA 18, PENNSYLVANIA[1]]

Pyrolytic Preparation of α-Carbalkoxyalkyl Acrylates and Methacrylates[1a]

BY E. M. FILACHIONE, J. H. LENGEL AND C. H. FISHER

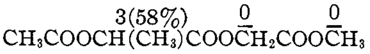
α-Carbalkoxyalkyl acrylates and methacrylates have been prepared by treating alkyl lactates with acrylyl chloride, methacrylyl chloride or methacrylic anhydride[2,3] and by heating potassium acrylate or methacrylate with methyl chloroacetate[3] or methyl α-bromobutyrate.[3] The acrylates and methacrylates of this type thus far prepared polymerize readily, and in this respect resemble the unsubstituted alkyl esters[4,5] of acrylic and methacrylic acid. The purpose of the present work was to devise an alternative method for making certain carbalkoxyalkyl acrylates (II) and methacrylates (IV) and to determine the relative thermal stabilities of the three ester groups present in the α-acetoxypropionates (I) and α-acetoxyisobutyrates (III) of hydroxy esters such as methyl lactate.

$$\underset{\mathrm{I}}{\mathrm{CH_3COOCH(CH_3)COOCH(CH_3)COOCH_3}} \xrightarrow[550^\circ]{500\text{ to}} \underset{\mathrm{II}}{\mathrm{CH_2{=}CHCOOCH(CH_3)COOCH_3}} + \mathrm{CH_3COOH}$$

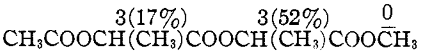
$$\underset{\mathrm{III}}{\mathrm{CH_3COOC(CH_3)_2COOCH(CH_3)COOR}} \xrightarrow[550^\circ]{450\text{ to}} \underset{\mathrm{IV}}{\mathrm{CH_2{=}C(CH_3)COOCH(CH_3)COOR}} + \mathrm{CH_3COOH}$$

The α-acetoxypropionates (I) and α-acetoxyisobutyrates (III) used in the pyrolysis experiments were made conveniently and in high yields by acylating methyl glycolate or alkyl lactate with acetoxypropionyl chloride or acetoxyisobutyryl chloride. One of the compounds (acetoxypropionate of methyl lactate, I) prepared in this manner and used in the present work had been made previously by treating methyl lactyllactate with acetic anhydride.[6]

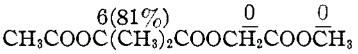
The acetoxy esters (I and III) were decomposed by passage through a Pyrex glass tube heated at temperatures ranging from 450 to 550°. Although each of the compounds pyrolyzed contained three esterified carboxyl groups, decomposition occurred preferentially at the carboxyl group esterified with the hydroxy acid having the largest number of hydrogen atoms on its beta-carbons. This relation between thermal stability and number of beta-hydrogen atoms was in agreement with previous observations,[7] and the acetoxy esters subjected to pyrolysis were selected (with the exception of α-carbomethoxyethyl α-acetoxypropionate, (I)) so that one ester group would have more beta-hydrogens than either of the other two. The number of β-hydrogen atoms and extent of cleavage for each ester group are shown below (per cent. yield of corresponding unsaturated ester or olefin used as measure of cleavage)



$\mathrm{CH_3COOCH}\overset{3(58\%)}{\mathrm{(CH_3)}}\mathrm{COO}\overset{0}{\mathrm{CH_2}}\mathrm{COO}\overset{0}{\mathrm{CH_3}}$ (V)



$\mathrm{CH_3COOCH}\overset{3(17\%)}{\mathrm{(CH_3)}}\mathrm{COOCH}\overset{3(52\%)}{\mathrm{(CH_3)}}\mathrm{COO}\overset{0}{\mathrm{CH_3}}$ (I)



$\mathrm{CH_3COOC}\overset{6(81\%)}{\mathrm{(CH_3)_2}}\mathrm{COO}\overset{0}{\mathrm{CH_2}}\mathrm{COO}\overset{0}{\mathrm{CH_3}}$ (VI)

$\mathrm{CH_3COOC}\overset{6(65\%)}{\mathrm{(CH_3)_2}}\mathrm{COOCH}\overset{3(8\%)}{\mathrm{(CH_3)}}\mathrm{COO}\overset{0}{\mathrm{CH_3}}$ (VII)

$\mathrm{CH_3COOC}\overset{6(58\%)}{\mathrm{(CH_3)_2}}\mathrm{COOCH}\overset{3(4\%)}{\mathrm{(CH_3)}}\mathrm{COO}\overset{3(3\%)}{\mathrm{CH_2CH_3}}$ (VIII)

The acetoxypropionate of methyl lactate (I) differed from the other acetoxy esters (V to VIII), in that two of its ester groups had the largest number of β-hydrogen atoms. Since pyrolysis of this ester (I) yielded much more methyl acrylate than carbomethoxyethyl acrylate (II), the acetate group was more stable than the acetoxypropionate group. This observation is in harmony with the fact that ethylene rather than ethyl acrylate is the principal product when ethyl α-acetoxypropionate is thermally decomposed.[8]

Acetone, ethyl acrylate, methacrylic acid and ethyl α-acetoxypropionate were obtained as by-products in the pyrolysis of the acetoxyisobutyrate of ethyl lactate (VIII). Presumably ethyl acrylate and α-acetoxyisobutyric acid (IX) were

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[1a] Presented at the Meeting in Miniature of the Philadelphia Section, A. C. S., June 13, 1945.

[2] C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **67**, 208 (1945).

[3] D. E. Strain, U. S. Patent 2,141,546, Nov. 27, 1938.

[4] H. T. Neher, *Ind. Eng. Chem.*, **28**, 267 (1936).

[5] C. E. Rehberg, W. A. Faucette and C. H. Fisher, THIS JOURNAL, **66**, 1723 (1944).

[6] H. V. Claborn, U. S. Patent 2,350,388, June 6, 1944.

[7] (a) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938); (b) C. D. Hurd, "The Pyrolysis of Carbon Compounds," Reinhold Publishing Corp., N. Y., 1929.

[8] R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935); C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **67**, 56 (1945).