dine (18 ml.), boiled at 103° (0.2 mm.) and 130° (2.0 mm.), n_D^{25} 1.5095, d_4^{25} 1.170, yield 10.1 g. (80%); reported b.p. 144–145° (2 mm.), n_D^{17} 1.5145, d_4^{17} 1.618.[9] A strong absorption band ascribable to the carbonyl function appeared at 1710 cm.$^{-1}$ in the infrared spectrum of the ester (liquid); there was no hydroxyl absorption.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; mol. wt., 222.2. Found: C, 65.12; H, 6.23; mol. wt. (ebullioscopic in acetone), 225.

From the sodium salt of III and methyl iodide in *N*-methylpyrrolidone, the methyl ether of III was synthesized, b.p. 49–50° (18 mm.), n_D^{25} 1.4128; reported b.p. 56–58° (23 mm.), n_D^{17} 1.4177.[9] The infrared spectrum (liquid) of the colorless derivative was consistent with its assigned structure, exhibiting no significant absorption above 3000 cm.$^{-1}$ A portion of the ether (1.24 g.; 0.0094 mole) was hydrolyzed in dilute acid as previously described. Periodate analysis[8] of the hydrolyzate showed that the solution contained a total of 0.0092 equivalent (98%) of vicinal hydroxyl functions.

(c) When the vinylation of glycerol was conducted as described in part (b) for a period of 7 hr. at 137–150°, the dioxolane II and the trivinyl ether I were obtained in 65 and 5% yield, respectively.

(9) The benzoate ester of III, prepared according to the procedure of Hill, Hill, and Hibbert (see Table I, footnate a), had a b.p. of 104° (0.24 mm.). It was shown to be identical with the derivative described above by a comparison of the infrared spectra and the other physical constants.

Continuous vinylation of glycerol in a condensed-phase coil reactor.[10] Under a pressure of 20 atm., *N*-methylpyrrolidone was saturated with acetylene at 12.0°. The solution was pumped continuously at a rate of 9.0 ml./min. under a pressure of 100–135 atm. (sufficient to prevent the formation of a vapor phase) through a tubular reactor heated to 190°. A solution of potassium hydroxide (7.9 wt.%) in glycerol was injected into the hot acetylene solution at a rate (3.2 ml./min.) such that the molar ratio of acetylene to glycerol was greater than 3:1. After a reaction time of 9.2 min., the reaction mixture passed out of the reactor through a pressure relief valve. The excess acetylene was vented and the product solution was added to twice its volume of water. The organic layer was separated and the aqueous layer was washed several times with ether. The products were isolated by fractional distillation under reduced pressure. Under these conditions, glycerol was converted to the trivinyl ether I (50%) and the dioxolane II (30%).

Acknowledgment. The authors wish to express their sincere appreciation to Dr. Newman M. Bortnick and Dr. Clayton M. Huggett for many helpful suggestions and constructive criticisms during the course of this work.

PHILADELPHIA, PA.

(10) J. J. Nedwick and C. M. Huggett, U. S. Pat. 2,969,400 (1961).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MEERUT COLLEGE]

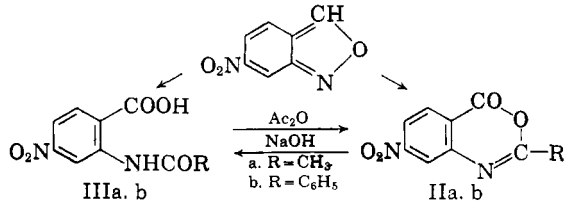
Behavior of Halogenated Nitrobenzenes with β-Diketones. II. 6-Nitroanthranil from 2,4-Dinitrophenylacetone

S. S. JOSHI AND I. R. GAMBHIR

Received March 10, 1961

6-Nitroanthranil, formed by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone, has been further characterized. Like anthranil, it adds to mercuric chloride, can be acetylated and benzoylated, but unlike anthranil itself it forms indazole derivatives with aniline, phenylhydrazine, and hydrazine acetate. The acyl derivatives can be transformed into *o*-acylaminobenzamides and subsequently to quinazolone derivatives.

In a previous communication[1] it was stated that the compound formed by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone may be 6-nitroanthranil (I). It has been further observed that like anthranil[2] the compound I with alcoholic mercuric chloride forms a molecular compound from which it is recovered with hot water. When heated with acetic anhydride and zinc acetate, it gives an acetyl derivative which is found to be identical with 4-nitroacetanthranil (or 7-nitro-2-methylbenzoxazone) (IIa), a product obtained by treatment of 4-nitroacetylanthranilic acid (IIIa) with acetic anhydride.[3] On heating with benzoyl chloride and pyridine, it yields 4-nitrobenzoylanthranil (or 7-nitro-2-phenylbenzoxazone) (IIb) and 4-nitro-*N*-benzoylanthranilic acid (IIIb), which are also obtained by benzoylation of 2-amino-4-nitrobenzoic acid. These compounds IIb and IIIb are interconvertible by treatment with acetic anhydride and dilute caustic soda solution respectively.[4]



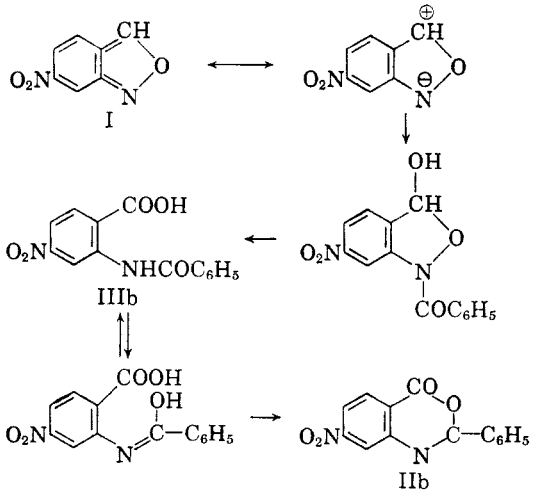
A simple mechanism for the formation of 4-nitrobenzoylanthranil (IIb) from 6-nitroanthranil (I) through 4-nitro-*N*-benzoylanthranilic acid (IIIb) as an intermediate, which is also isolated, is given as follows:

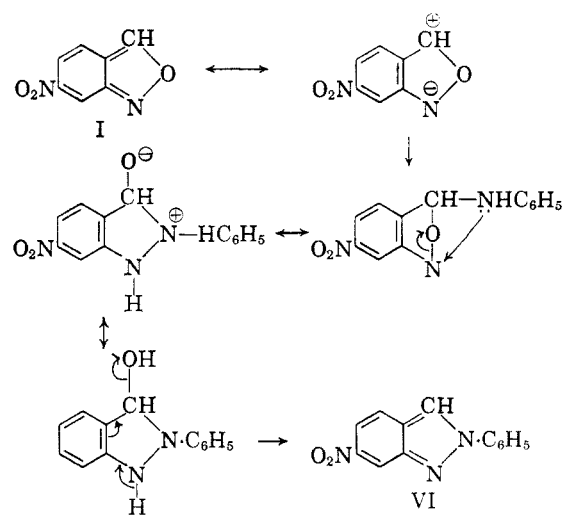
(1) *J. Am. Chem. Soc.*, **78**, 2222 (1956).

(2) O. Buhlmann and A. Einhorn, *Ber.*, **34**, 3788 (1901).

(3) M. T. Bogert and S. H. Steiner, *J Am. Chem. Soc.*, **27**, 1330 (1905).

(4) P. Ruggli and W. Leonhardt, *Helv. Chim. Acta*, **7**, 808 (1926).





The nitroacylanthranils when heated with primary amines[5,6] give *o*-acylaminonitrobenzamides; these are reported to cyclize to quinazolones when R represented an alkyl group and not when R was an aryl one.[7] The latter can also be cyclized when heated alone above their melting points. Following this procedure a few 2-phenylquinazolones have been obtained from *o*-arylaminonitrobenzamides synthesized from 4-nitrobenzoylanthranil and ammonia, aniline, toluidines, etc.

When heated with hydrazine acetate and hydroxylamine in glacial acetic acid, 4-nitrobenzoylanthranil is directly converted into 3-amino-7-nitro-2-phenyl-4-quinazolone (IV) and 3-hydroxy-7-nitro-2-phenyl-4-quinazolone (V), respectively; no intermediate *o*-arylaminonitrobenzamides could be isolated. The aminoquinazolone is basic in character while the hydroxy derivative is acidic. Both of them form acetyl and benzoyl derivatives. They are recovered unchanged from their salts with concentrated hydrochloric acid and caustic soda respectively when made alkaline or acidic.

6-Nitroanthranil (I) when heated with aniline at 150° forms 6-nitro-2-phenylindazole (VI), but unlike anthranil it neither gives the anilide of 4-nitro-2-aminobenzaldehyde nor any other compound.[8] The compound VI is soluble in concentrated hydrochloric acid and is reprecipitated on dilution. A simple mechanism for its formation is given.

6-Nitroanthranil (I) when heated with hydrazine acetate in glacial acetic acid forms 6,6′-dinitrobisindazolyl (VII) and with phenylhydrazine alone or in alcoholic solution yields 6-nitro-2-anilinoindazole (VIII). Unlike anthranil itself[9] it does not react with the latter reagent to form the phenylhydrazone of nitroaminobenzaldehyde or an additive compound. Both compounds VII and VIII dissolve in concentrated hydrochloric acid and are precipitated from their solutions on dilution or addition of an alkali.

EXPERIMENTAL

Mercuric chloride compound of I. A solution of 6-nitroanthranil (I) (0.5 g.) in alcohol (5 ml.) and mercuric chloride (1.3 g.) in alcohol (15 ml.) was refluxed for an hour. On cooling a yellow product separated which on recrystallization from alcohol gave 0.95 g. of the mercuric chloride compound of I, pale yellow needles, m.p. 158°.

Anal. Calcd. for $C_7H_4N_2O_3$: $HgCl_2$: Cl, 16.32. Found: Cl, 15.96.

4-Nitroacetanthranil (7-nitro-2-methylbenzoxazone) (IIa) *and 4-nitro-N-acetylanthranilic acid* (IIIa). Compound I (0.5 g.), acetic anhydride (6 ml.) and zinc acetate (0.1 g.) in glacial acetic acid (2 ml.) were refluxed for 4 hr. On cooling crystals separated which on recrystallization from acetic acid gave 0.3 g. of 4-nitroacetylanthranil, as pale yellow cubes, m.p. 138°.

Anal. Calcd. for $C_9H_6N_2O_4$: C, 52.42; H, 2.91. Found: C, 52.10; H, 2.88.

The mother liquor on concentration gave more of IIa (0.05 g.). The filtrate on addition of water yielded a semi-solid mass which on purification with activated charcoal and recrystallization from dilute acetic acid gave 0.2 g. of 4-nitro-*N*-acetylanthranilic acid, colorless needles, m.p. 217°.

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.21; H, 3.57. Found: C, 48.03; H, 3.53.

4-Nitrobenzoylanthranil (7-nitro-2-phenylbenzoxazone) (IIb) *and 4-nitro-N-benzoylanthranilic acid* (IIIb). A. Compound I (0.5 g.), benzoyl chloride (4.0 ml.) and few drops of pyridine were heated at 130° for 3 hr. On cooling yellow crystals separated; recrystallization from acetic acid gave 0.44 g. of 4-nitro-benzoylanthranil, colorless needles, m.p. 179°.

Anal. Calcd. for $C_{14}H_8N_2O_4$: C, 62.68; H, 2.98; N, 10.44. Found: C, 62.34; H, 2.92; N, 10.41.

The mother liquor was concentrated under reduced pressure and the residue on recrystallization from dilute alcohol gave 0.32 g. of 4-nitro-*N*-benzoylanthranilic acid, colorless needles, m.p. 252°.

Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.50. Found: C, 58.60; H, 3.42.

B. 4-Nitroanthranilic acid (1.0 g.), benzoyl chloride (8 ml.), and a few drops of pyridine were heated at 130° for 3 hr. On cooling a solid mass separated which on recrystal-

(5) R. Anschütz and O. Schmidt, *Ber.*, **35**, 3480 (1902).
(6) M. T. Bogert and S. H. Steiner, *J. Am. Chem. Soc.*, **27**, 1330 (1905). Bogert and H. A. Seil, *J. Am. Chem. Soc.*, **28**, 884 (1906); Bogert and W. Klaber, *J. Am. Chem. Soc.*, **30**, 807 (1908).
(7) R. Anschütz and O. Schmidt, *Ber.*, **35**, 3480 (1902).
(8) G. Heller and E. Grünthal, *Chem. Zentr.*, 975 (1910).
(9) O. Buhlmann and A. Einhorn, *Ber.*, **34**, 3788 (1901).

TABLE I

BENZANILIDES FROM 4-NITROBENZOYLANTHRANIL

No.	4-Nitro-2-benzoylaminobenz-	M.P.	Color	Yield, %	Calcd., %	Found, %
1	*o*-toluidide	205	Slate	68	C 67.20	66.91
					H 4.53	4.56
2	*m*-toluidide	202	Yellow	67	C 67.20	66.68
					H 4.53	4.50
3	*p*-toluidide	232	Colorless	70	C 67.20	67.01
					H 4.53	4.56
4	*o*-chloroanilide	217	Colorless	60	C 60.68	60.28
					H 3.53	3.57
5	*m*-chloroanilide	260	Yellow	62	C 60.68	60.46
					H 3.53	3.49
6	*p*-chloroanilide	236	Dirty yellow	66	C 60.68	60.41
					H 3.53	3.58
7	naphthylamide	263	Colorless	67	C 70.07	69.59
					H 4.13	4.11
8	naphthylamide	244	Yellow	71	C 70.07	69.72
					H 4.13	4.18

TABLE II

QUINAZOLONES FROM 4-NITRO-2-BENZOYLAMINOBENZAMIDES (TABLE I)

No.	7-Nitro-2-phenyl-3-4-quinazolone	M.P.	Color	Yield, %	Calcd., %	Found, %
1	3-*o*-toluidide-	154	Dirty white	47	C 70.58	70.26
					H 4.20	4.15
2	3-*m*-toluidide-	148	Colorless	49	C 70.58	70.19
					H 4.20	4.25
3	3-*p*-toluidide-	168	Pale yellow	50	C 70.58	70.37
					H 4.20	4.18
4	3-*o*-chlorophenyl-	164	Colorless	39	C 63.57	63.28
					H 3.17	3.13
5	3-*m*-chlorophenyl-	161	Buff	39	C 63.57	63.17
					H 3.17	3.20
6	3-*p*-chlorophenyl-	173	Colorless	41	C 63.57	63.33
					H 3.17	3.22
7	3-naphthyl-	194	Colorless	50	C 73.28	73.01
					H 3.81	3.79
8	3-naphthyl-	205	Colorless	54	C 73.28	72.97
					H 3.81	3.77

lization from alcohol gave 0.82 g. (IIb), colorless needles, m.p. 179°. The mother liquor on dilution gave a precipitate which on recrystallization from dilute acetic acid gave 0.61 g. (IIIb), colorless needles, m.p. 252°. The mixed melting points of IIb and IIIb obtained by both the methods (A) and (B) remained undepressed.

4-Nitro-2-benzoylaminobenzamide. A solution of IIb (0.5 g.) in absolute alcohol (10 ml.) was boiled under reflux and dry ammonia passed into it. A white crystalline mass separated which on recrystallization from acetic acid gave 0.46 g. of 4-nitro-2-benzoylaminobenzamide, colorless needles, m.p. 236°.

Anal. Calcd. for $C_{14}H_{11}N_3O_4$: C, 58.94; H, 3.86. Found: C, 59.01; H, 3.82.

On treatment with nitrous acid and also on warming with dilute caustic soda and subsequent acidification, it gave 4-nitro-*N*-benzoylanthranilic acid (IIIb).

7-Nitro-2-phenyl-4-quinazolone. Nitrobenzoylaminobenzamide obtained above (0.5 g.) was heated at 250° for one-half hour. The dark brown product was washed with hot alcohol and the residue extracted with a mixture of alcohol and ethyl acetate. The extract after purification with activated charcoal gave 0.28 g. of 7-nitro-2-phenyl-4-quinazolone, yellow cubes, m.p. 329°.

Anal. Calcd. for $C_{14}H_9N_3O_3$: C, 62.92; H, 3.37. Found: C, 62.48; H, 3.32.

4-Nitro-2-benzoylaminobenzanilide. Compound IIb (0.5 g.) and aniline (3 ml.) were heated at 150° for 2 hr. The product after washing with dilute hydrochloric acid and recrystallizing from acetic acid gave 0.48 g. of 4-nitro-2-benzoylaminobenzanilide, colorless needles, m.p. 228°.

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.15. Found: C, 66.19; H, 4.12.

7-Nitro-2,3-diphenyl-4-quinazolone. 4-Nitro-2-benzoylaminobenzanilide (0.5 g.) was heated at 250° for one-half hour. The product was extracted with alcohol which after purification with activated charcoal gave 0.25 g. of 7-nitro-2,3-diphenyl-4-quinazolone, colorless needles, m.p. 180°.

Anal. Calcd. for $C_{20}H_{13}N_3O_3$: C, 69.97; H, 3.79. Found: C, 69.79; H, 3.75.

4-Nitro-2-benzoylaminobenzphenylhydrazide. Compound IIb (0.5 g.) and phenylhydrazine (4 ml.) were heated on water bath for 2 hr. The contents after washing with dilute hydrochloric acid and recrystallizing from dilute alcohol gave 0.51 g. of 4-nitro-2-benzoylaminobenzphenylhydrazide, cream-colored needles, m.p. 185°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.83; H, 4.25. Found: C, 63.51; H, 4.17.

3-Anilino-7-nitro-2-phenyl-4-quinazolone. 4-Nitro-2-benzoylaminobenzphenylhydrazide (0.4 g.) was heated at 220° for 1 hr. The product was extracted with alcohol which after purification with activated charcoal gave from

dilute alcohol 0.18 g. of 3-anilino-7-nitro-2-phenyl-4-quinazolone, colorless needles, m.p. 151°.

Anal. Calcd. for $C_{20}H_{14}N_4O_3$: C, 67.04; H, 3.91. Found: C, 66.83; H, 3.85.

A few *o*-acylaminobenzanilides were obtained from 4-nitro-benzoylanthranil (IIb) and aromatic amino compounds (Table I). These gave the corresponding quinazolone derivatives when heated about 30° above their melting points (Table II).

3-Amino-7-nitro-2-phenyl-4-quinazolone (IV). A solution of IIb (0.5 g.) in glacial acetic acid (10 ml.) and hydrazine hydrate (4.0 ml.) was refluxed for 1 hr. On cooling pale yellow crystals separated which on recrystallization from dilute acetic acid gave 0.46 g. of IV, lemon-yellow needles, m.p. 249°

Anal. Calcd. for $C_{14}H_{10}N_4O_3$: C, 59.57; H, 3.54; N, 19.85. Found: C, 59.25; H, 3.50; N, 20.00.

Benzoyl derivative of IV. Colorless cubes from alcohol and ethyl acetate mixture, m.p. 295°.

Anal. Calcd. for $C_{21}H_{14}N_4O_4$: C, 65.28; H, 3.62. Found: C, 64.81; H, 3.60.

Acetyl derivative of IV. Colorless plates from alcohol, m.p. 149°.

Anal. Calcd. for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.70. Found: C, 58.92; H, 3.67.

3-Hydroxy-7-nitro-2-phenyl-4-quinazolone (V). Prepared by the procedure given for compound IV by using hydroxylamine hydrochloride and sodium acetate. Recrystallization from dilute acetic acid gave 70% of V, colorless cubes, m.p. 246°.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.36; H, 3.18. Found: C, 59.01; H, 3.16.

Benzoyl derivative of V. Light brown needles from dilute alcohol, m.p. 273°.

Anal. Calcd. for $C_{21}H_{13}N_3O_5$: C, 65.11; H, 3.35. Found: C, 64.92; H, 3.30.

Acetyl derivative of V. Colorless cubes from dilute acetic acid, m.p. 157°.

Anal. Calcd. for $C_{16}H_{11}N_3O_5$: C, 59.07; H, 3.38. Found: C, 58.86; H, 3.39.

6-Nitro-2-phenylindazole (VI). Compound I (0.5 g.) and aniline (4 ml.) were heated at 140° for 3 hr. On cooling orange yellow cubes separated which on recrystallization from acetic acid gave 0.30 g. of VI, orange-yellow needles, m.p. 325°

Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.76. Found: C, 64.89; H, 3.70.

6,6'-Dinitro-2,2'-bisindazolyl (VII). Compound I (0.5 g.) in glacial acetic acid (10 ml.) and hydrazine hydrate (4 ml.) were refluxed for 2 hr. On cooling reddish brown needles separated which on recrystallization from ethyl acetate gave 0.35 g. of VII, orange needles, m.p. 324°.

Anal. Calcd. for $C_{14}H_8N_6O_4$: C, 51.85; H, 2.47; N, 25.93. Found: C, 51.48; H, 2.81; N, 25.80.

6-Nitro-2-anilinoindazole (VIII). Compound I (0.5 g.) and phenylhydrazine (3 ml.) were heated on water bath for 3 hr. The product after washing with dilute hydrochloric acid, alcohol, and recrystallizing from acetic acid gave 0.41 g. of VIII, reddish brown needles, m.p. 190°.

Anal. Calcd. for $C_{13}H_{10}N_4O_2$: C, 61.42; H, 3.94. Found: C, 61.20; H, 4.00.

MEERUT, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF SYNTHETIC ORGANIC CHEMISTRY, MEAD JOHNSON RESEARCH CENTER, MEAD JOHNSON AND CO.]

Syntheses Pertaining to the Carbamoylation of Cyclic 1,3-Dicarbonyl Compounds with Urea

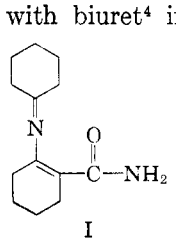
HOMER C. SCARBOROUGH

Received March 1, 1961

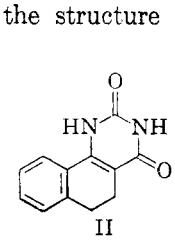
The mechanism of carbamoylation of cyclic 1,3-dicarbonyl compounds with urea is discussed with respect to the reactions of urea and derivatives with carbonyl compounds. These are the reactions of cyclohexanone and 2-methyl cyclic 1,3-dicarbonyl compounds with urea and the reactions of 1,3-dimethylbarbituric acid with urea and derivatives. A bicyclic transition state mechanism is suggested as a possibility by which these results may be interpreted.

The carbamoylation of some cyclic 1,3-dicarbonyl compounds with urea has been reported as has been a rationale for the use of urea as a source of the elements of cyanic acid in this reaction.[1,2] As the synthesis is accomplished at elevated temperatures, it was felt that free cyanic acid might be an actual reacting species and a cyclic transition state was suggested.[1] A number of active methylene compounds were treated with urea; however, only cyclic 1,3-dicarbonyl compounds gave simple carbamoyl derivatives. Cyclohexanone furnished a carbamoyl compound in which the keto carbonyl was replaced by imine function.[2,3]

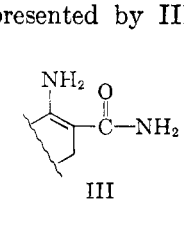
The formation of cyclohexylidene 2-carbamoylcyclohex-1-enylamine, I, from the reaction of cyclohexanone[2,3] or 1(*N*-morpholino)cyclohexene[2] and urea would appear to be analogous to the preparation of compound II which has been reported by the fusion of α-tetrolone with urea or with biuret[4] if the structure represented by III



I



II



III

(1) H. C. Scarborough, *J. Org. Chem.*, **26**, 2579 (1961).

(2) H. C. Scarborough and W. A. Gould, *J. Org. Chem.*, **26**, 3720 (1961).

(3) A. F. McKay, E. J. Tarlton, and C. Podesva, *J. Org. Chem.*, **26**, 77 (1961).

(4) K. Dziewonski and J. Schoen, *Bull. intern. acad. polon. sci., Classe sci. mathl nat.*, Ser. A. 101 (1950); *Chem. Abstr.*, **47**, 136h (1953).