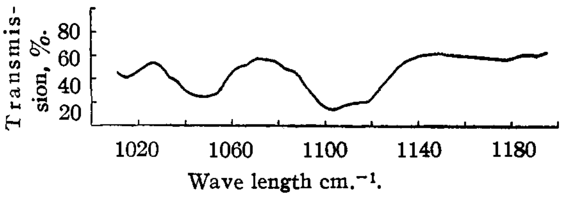

Fig. 1.—Infrared spectrum of (II): 0.045 g. in 1 cc. of chloroform; cell thickness 0.1 mm.

band of the acetal spectrum. This interpretation was confirmed by the investigation of ethyl orthoformate and orthobenzoate (Fig. 2, 3) which absorb in the infrared at similar wave lengths and with a similarly high intensity of the third band (ϵ = molecular extinction coefficient for 1 mole per cc. and 1 mm. cell thickness):

Compound (II): 1178 ($\epsilon = 1 \times 10^4$)−1118[shoulder] (4×10^4)−1103(8×10^{-4})−1048 cm.$^{-1}$(6×10^4); ethyl orthoformate: 1159 ($\epsilon = 2 \times 10^4$)−1125(2.5×10^4) −1092(10×10^4)−1059 cm.$^{-1}$(6×10^4); ethyl orthobenzoate: 1163 ($\epsilon = 1 \times 10^4$)−1108(3.5×10^4)−1081·(6×10^4)−1036 cm.$^{-1}$(4×10^4).

In addition, the spectrum of (II) shows a band at 1015 cm.$^{-1}$, and the spectrum of ethyl orthobenzoate three bands at 1145, 1060 and 1015 (shoulder) cm.$^{-1}$.

Pentaerythritol tetraacetate, which has been studied for comparison, shows in the region investigated, only a single peak, at 1042 cm.$^{-1}$.

It is worthy of note that in contradistinction with the transition from ethers to acetals, the addition, in the ortho-esters, of the third oxygen atom does not cause a splitting of the bands, but only increases considerably the intensity of the third band.

The formation of the ortho-ester (II) is undoubtedly favored by the compactness of its molecule which is evident from a model. It is worth recalling that nitrotrimethylolmethane gives a very similar product (III), on treatment with phosphorus oxychloride.[3]

Esterification of pentaerythritol with *p*-nitrobenzoyl chloride gives the normal tetra-*p*-nitrobenzoate, whilst (II) is not attacked by the acid chloride. (II) can, therefore, not be an intermediate in the formation of the tetraester.

Experimental

Pentaerythritol Mono-(*p*-nitrobenzoate) Ortho-(*p*-nitrobenzoate) (II).—To a suspension of (I)[4] (15.6 g.) in glacial acetic acid (100 cc.), 4-nitrophenylhydrazine (4.6 g.) and concentrated hydrochloric acid (5 cc.) were added. A clear solution formed which deposited quickly crystals of benzaldehyde 4-nitrophenylhydrazone in quantitative yield (m.p. 189°, after recrystallization). The filtrate was diluted with 100 cc. of alcohol, cooled at 0° and induced to crystallization by scratching with a glass-rod. The compound (II) was washed with methanol and recrystallized from benzene or glacial acetic acid. It formed prisms of m.p. 137–138°; yield 10 g. (80%).

Anal. Calcd. for $C_{19}H_{16}O_9N_2$: C, 54.8; H, 3.9; N, 6.7. Found: C, 54.9; H, 4.1; N, 6.6.

Pentaerythritol Tetra-(*p*-nitrobenzoate).—A solution of 1.36 g. of pentaerythritol in pyridine was heated at 100° with 7.5 g. of *p*-nitrobenzoyl chloride for two hours and then poured into cold dilute sulfuric acid. The solid was washed with sodium carbonate solution, water and acetone, and the product (7 g., 95%) recrystallized from glycol monoacetate. It melted at 215°.

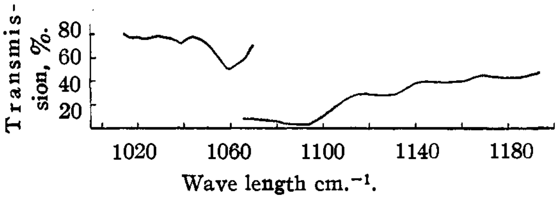

Fig. 2.—Infrared spectrum of ethyl orthoformate: left curve, 0.095 g. in 1 cc. of carbon tetrachloride; right curve, 0.043 g. in 1 cc. of chloroform; cell thickness 0.1 mm.

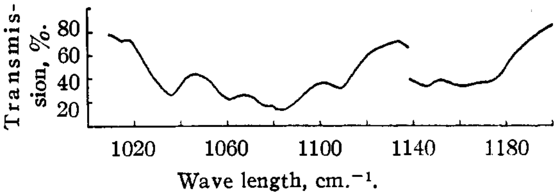

Fig. 3.— Infrared spectrum of ethyl orthobenzoate: left curve, 0.031 g., right curve, 0.092 g. in 1 cc. of carbon tetrachloride; cell thickness 0.1 mm.

Anal. Calcd. for $C_{33}H_{24}O_{16}N_4$: N, 7.6. Found: N, 7.6.

Ethyl orthobenzoate was prepared according to Limpricht[5]; b.p. 131–132° (17 mm.).

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[3] Zetzsche and Zurbruegg, *Helv. Chim. Acta*, **9**, 297 (1926).

[4] Bograchov, This Journal, **72**, 2268 (1950).

[5] Limpricht, *Ann.*, **135**, 87 (1865).

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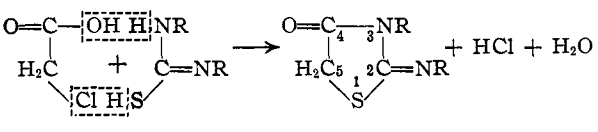
Received October 26, 1950

The Synthesis of Some 3-Aryl-2-arylimino-4-thiazolidones

By Prithwi Nath Bhargava

Desai, Hunter and Koppar[1] prepared 3-phenyl-2-phenylimino-4-thiazolidone. The preparation of some 3-aryl-2-arylimino-4-thiazolidones has been reported by Dains, Irvin and Harrel.[2] Klare, Markley and Reid[3] have further studied the conditions for the preparation of this type of compound by condensing diphenylthiourea and monochloroacetic acid in the presence of ethanol and sodium acetate by means of the reaction.



This reaction has now been extended to the synthesis of some 3-aryl-2-arylimino-4-thiazolidones not described as yet in the literature, by the condensation of the corresponding symmetrical diaryl thioureas with monochloroacetic acid in the presence of absolute ethanol and anhydrous sodium acetate. The structure of the thiazolidones is apparent from the method of preparation, and the formation of semicarbazones of the respective compounds gives evidence of the presence of a keto-group. The compounds are listed in Table I.

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[1] Desai, Hunter and Koppar, *Rec. trav. chim.*, **54**, 118 (1935).

[2] Dains, Irvin and Harrel, This Journal, **43**, 613 (1921).

[3] Klare, Markley and Reid, *ibid.*, **52**, 2137 (1930).

TABLE I

3-ARYL-2-ARYLIMINO-4-THIAZOLIDONES AND THEIR SEMICARBAZONES

Imino-4-thiazolidones	Yield, %	M.p., °C.	Formula	Analyses Nitrogen, % Calcd.	Nitrogen, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3-α-Naphthyl-2-α-naphthyl-	82	172–173[a]	$C_{23}H_{16}N_2OS$	7.60	7.62	75.00	75.22	4.34	4.32
3-β-Naphthyl-2-β-naphthyl-	80	192–193[a]	$C_{23}H_{16}N_2OS$	7.60	7.56	75.00	75.26	4.34	4.33
3-*p*-Anisyl-2-*p*-anisyl-	82.5	107–108[b]	$C_{17}H_{16}N_2O_3S$	8.53	8.56	62.19	62.22	4.87	4.85
3-*p*-Phenetyl-2-*p*-phenetyl-	84	105–106[b]	$C_{19}H_{20}N_2O_3S$	7.86	7.84	64.04	64.12	5.61	5.60
Semicarbazones of imino-4-thiazolidones									
3-α-Naphthyl-2-α-naphthyl-	94	180[b]	$C_{24}H_{19}N_5OS$	16.47	16.45	67.76	67.80	4.47	4.46
3-β-Naphthyl-2-β-naphthyl-	90	200[b]	$C_{24}H_{19}N_5OS$	16.47	16.50	67.76	67.82	4.47	4.45
3-*p*-Anisyl-2-*p*-anisyl-	88	120[c]	$C_{18}N_{19}N_5O_3S$	18.18	18.26	56.10	56.30	4.93	4.94
3-*p*-Phenetyl-2-*p*-phenetyl-	84	110[d]	$C_{20}H_{23}N_5O_3S$	16.95	16.98	58.11	58.20	5.57	5.60

[a] After recrystallization from chloroform. [b] After recrystallization from absolute ethanol. [c] After recrystallization from benzene. [d] After recrystallization from ethanol.

Experimental

Preparation of Starting Materials.—The chemicals were obtained as follows: α-naphthylamine, β-naphthylamine, *p*-anisidine and *p*-phenetidine were obtained from Eastman Kodak Company, and monochloroacetic acid from Merck and Co., Inc. The compounds S-di-α-naphthylthiourea, S-di-β-naphthylthiourea, S-di-*p*-phenetylthiourea and S-di-*p*-anisylthiourea were prepared by the method of Rathke.[4] The homogeneity of each compound was established by conventional methods (b.p., m.p., etc.), before using it in the reaction. In all cases the physical constants of the disubstituted thioureas were in good agreement with the values given in the literature.

Preparation of 3-Aryl-2-arylimino-4-thiazolidones. General Procedure.—A mixture consisting of 0.02 mole of diaryl thiourea, 0.03 mole of monochloroacetic acid and 0.06 mole of anhydrous sodium acetate in 50 ml. of absolute ethanol was refluxed for two hours on the steam-bath. Toward the end of the condensation, some of the compound separated in leaflets. The crude reaction mixture was distilled to remove excess ethanol and poured into water to remove sodium chloride produced in the reaction and excess sodium acetate. The mixture was filtered, and the residue dried and crystallized from absolute ethanol. The melting point listed in the accompanying table remained unchanged on recrystallization from absolute ethanol or chloroform.

Preparation of Semicarbazones. General Procedure.—A mixture consisting of 0.001 mole of 3-aryl-2-arylimino-4-thiazolidone, 0.003 mole of semicarbazide hydrochloride and 0.006 mole of crystalline sodium acetate in 20 ml. of 95% ethanol was heated on the steam-bath for 15 minutes. The reaction mixture was poured into 50 ml. of water and filtered. The residue was washed with cold water, dried and crystallized from absolute ethanol or benzene for purposes of establishing melting point and analytical data, Table I.

Acknowledgment.—The author is indebted to the Uttar Pradesh Government Scientific Research Committee for a grant, which made this work possible and also to the authorities of the Banaras Hindu University for providing facilities in the Laboratory of Organic Chemistry.

[4] Rathke, *Ber.*, **6**, 799 (1873).

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RECEIVED JANUARY 3, 1951

Derivatives of 2,4-Diphenylbutylamine and 2,4-Diphenylpyrrolidine

BY F. G. BORDWELL AND MARTIN KNELL[1]

In connection with another problem we wished to prepare 2,4-diphenylbutylamine. According to a report by Adkins and Whitman[2] this compound was obtained by the reduction of 4-nitro-1,3-diphenyl-1-butanone in dioxane solution with hydrogen and Raney nickel at 70–126° under a pressure of 150 atmospheres. Recently Kloetzel[3] reduced the same compound under similar conditions in methanol and described the product as 2,4-diphenylpyrrolidine. These investigators[2,3] apparently obtained similar products, since each reported the preparation of a phenylthiourea derivative melting at nearly the same point (191–191.5° *vs.* 189–190°).

Previous to these accounts Kohler and Drake[4] had obtained small quantities of the hydrochloride (m.p. 171–172°) and oxalate of 2,4-diphenylpyrrolidine by reduction of 4-nitro-1,3-diphenyl-1-butanone with hydrogen and a platinum catalyst. Identification was made on the basis of carbon and hydrogen analyses; there is usually a significant difference in the hydrogen content of derivatives of 2,4-diphenylpyrrolidine and 2,4-diphenylbutylamine, but not in the carbon or nitrogen content. Rupe and Gisiger[5] also isolated a small amount of the oxalate of 2,4-diphenylpyrrolidine from the reduction of 2,4-diphenyl-4-oxobutanenitrile with hydrogen and a large quantity of nickel catalyst. Carbon and hydrogen analyses were given for the oxalate and free base. From their base they prepared a hydrochloride (m.p. 154°) and a phenylthiourea (m.p. 188°) for which they gave nitrogen analyses.

Adkins and Whitman[2] made their structure assignment as a primary amine on the basis of the formation of a 3-nitrophthalimide[6] (in unstated yield). Kloetzel[3] claimed the absence of primary amines in the products from his reductions of γ-nitroketones in view of the failure of any portion of the benzenesulfonamides to dissolve in 10% aqueous sodium hydroxide. However, the benzenesulfonamides of many aryl–aliphatic primary amines are insoluble in aqueous alkali.[7] Neither Adkins and Whitman[2] nor Kloetzel[3] reported hydrogen analyses for their bases or derivatives. Kloetzel pointed out the similarity in melting point of the phenylthiourea (189–190°) to that given by Rupe and Gisiger[5] for the phenylthiourea of 2,4-diphenylpyrrolidine (188°), and the similarity in melting point of the

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[1] National Institute of Health Predoctoral Fellow, 1947–1948.

[2] Adkins and Whitman, THIS JOURNAL, **64**, 150 (1942).

[3] Kloetzel, *ibid.*, **69**, 2271 (1947).

[4] Kohler and Drake, *ibid.*, **45**, 2144 (1923).

[5] Rupe and Gisiger, *Helv. Chim. Acta*, **8**, 349 (1925).

[6] Alexander and McElvain, THIS JOURNAL, **60**, 2285 (1938).

[7] Carothers, Bickford and Hurwitz, *ibid.*, **49**, 2908 (1927).