Studies on Meso-ionic Compounds. XIII[1]. *ψ-2, 4-Dihydro-4, 5-diphenyl-2-keto-1-oxa-3, 4-diazole**

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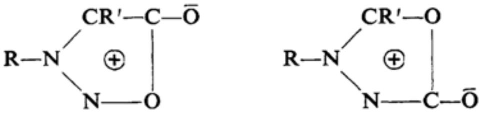
Since Earl et al.[2] synthesized in 1935 3-phenylsydnone (I; R=Ph, R′=H), many studies on meso-ionic compounds have been carried out especially with sydnones I, whereas not any meso-ionic compound of type II which differs from the sydnones in the reversal of the -CO-O- grouping is yet known, and we have therefore undertaken a general study of this new meso-ionic system.

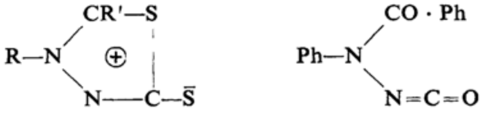


I II

VI; R=R′=C_6H_5
IX; R=CH_3, R′=C_6H_5

Fig. 1

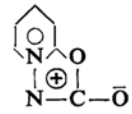
Attempts to prepare the compound II were already made by Baker et al.[3] in 1950. Their attempts were mainly based on methods by which the dithio-analogues III had been prepared[4], and the failure of their syntheses was due in several cases to the instability of carbamic acids. On the assumption that iso-cyanate IV might cyclise to the compound II, the reaction of the hydrochloride of *N*-benzoyl-*N*-phenylhydrazine with carbonyl chloride in boiling toluene was also tried, but they obtained *N, N′*-di(benzanilido)urea alone.



III IV

Fig. 2

On the other hand, Hoegerle[5] reported that *N*-aminopyridone-(2) was subjected to the action of carbonyl chloride in chloroform in the presence of potassium carbonate to give the compound V in which the meso-ionic ring in question forms part of a polycyclic system.



V

Fig. 3

Now we treated *N*-benzoyl-*N*-phenylhydrazine with carbonyl chloride under the same conditions as Hoegerle used and recrystallized the product from dry benzene obtaining a crystalline solid $C_{48}H_{36}O_6N_6$, m. p. 161~162°C. This, if formulated as $3\cdot C_{14}H_{10}O_2N_2$, C_6H_6, would correspond to the required meso-ionic compound VI incorporating benzene. Heating the crystalline solid at 100°C under reduced pressure for four days removed benzene from it to afford white crystals, m. p. 165~166°C, which gave analytical figures indicative of the formula $C_{14}H_{10}O_2N_2$.

A comparison of the infrared spectrum of the compound with that of its precursor, *N*-benzoyl-*N*-phenylhydrazine, led us to assign it the structure VI. That is: (1) the disappearance of bands at 3338 and 3278 cm^{-1} in the precursor, arising from NH stretching, (2) the lack of the characteristic band for iso-cyanate group, and (3) the shift of Amide I band in the precursor at 1625 cm^{-1} towards a band at 1755 cm^{-1}, which corresponds closely with the ester-carbonyl bands in sydnones listed by Earl et al.[6] and Fugger et al.[7] We therefore designated the compound VI as ψ-2, 4-dihydro-4, 5-diphenyl-2-keto-1-oxa-3, 4-diazole following the systematic nomenclature proposed by Baker et al.[8]

The ψ-oxadiazole VI is insoluble in absolute ethanol at room temperature, but on heating it converts into ethyl *N*-benzoyl-*N*-phenylhydrazinoformate (VII). When refluxed with cyclohexanol in dry benzene for 6 hr. VI gives

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[1] Part XII: M. Hashimoto and M. Ohta, This Bulletin, 33, 1394 (1960).

* Presented at the Local Meeting of the Chemical Society of Japan, Hokkaido, July, 1960.

[2] J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, **1935**, 899.

[3] W. Baker, W. D. Ollis and V. D. Poole, ibid., **1950**, 1547.

[4] M. Busch et al., *Ber.*, **28**, 2635 (1895); *J. pr. Chem.*, **60**, 218, 228, 231, 236 (1899); **67**, 201, 202, 246, 250, 257 (1903); W. Baker et al., *J. Chem. Soc.*, **1951**, 289.

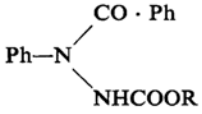
[5] K. Hoegerle, *Helv. Chim. Acta*, **41**, 548 (1958).

[6] J. C. Earl et al., *J. Chem. Soc.*, **1951**, 2207.

[7] J. Fugger et al., *J. Am. Chem. Soc.*, **77**, 1845 (1955).

[8] W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1949**, 311.

cyclohexyl *N*-benzoyl-*N*-phenylhydrazinoformate (VIII). Heating VI with *N*-benzoyl-*N*-phenylhydrazine at 100°C for 20 min. affords



VII; $R=C_2H_5$
VIII; $R=C_6H_{11}$

Fig. 4

N, *N'*-di(benzanilido)urea, which has a lower melting point by 10°C than that reported by Baker et al., but gives the correct analytical values. The same product is also obtained on treatment of VI with boiling water for 3 hr. When heated with aniline at 100°C for 15 min., VI gives 1-benzoyl-1, 4-diphenylsemicarbazide. On treatment with concentrated aqueous ammonia or aqueous dimethylamine, VI gives not the corresponding semicarbazides, but benzamide or *N*-benzoyl-*N*-phenylhydrazine, respectively.

These reactions which suggest the presence of a iso-cyanate group in a molecule were also observed in the polycyclic analogue V⁵⁾. However, the fact that V can be recrystallized from ethanol but VI suffers a ring fission from hot ethanol indicates that VI is less stable than V.

By acid hydrolysis, VI regenerates *N*-benzoyl-*N*-phenylhydrazine. The probable mechanism of the above described hydrolysis is shown in

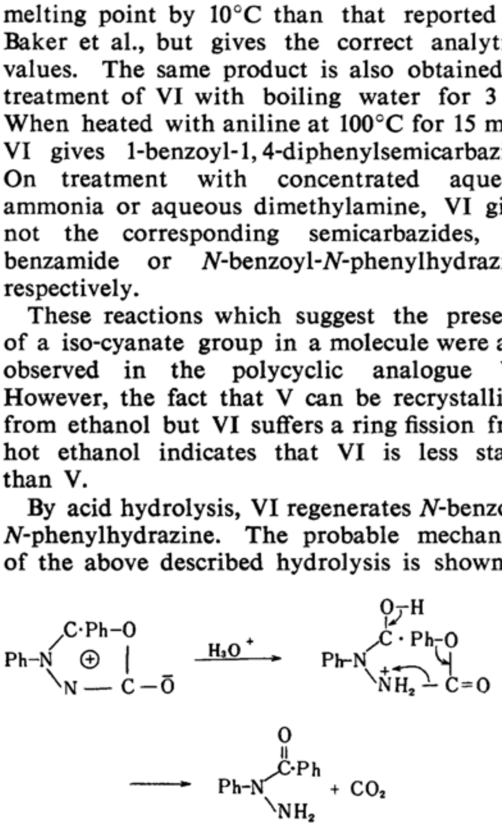


Fig. 5

Fig. 5 after that of acid hydrolysis of sydnones proposed by Baker et al.⁹⁾ Unlike sydnones**, *N*-benzoyl-*N*-phenylhydrazine obtained here is unaffected by acid and therefore no further degradation towards phenylhydrazine and benzoic acid might occur.

By alkaline hydrolysis, VI affords phenylhydrazine and benzoic acid. This observation could best be accounted for, if it is considered that the hydrolysis of lactonic group of VI produces unstable intermediate *N'*-carboxy-*N*-benzoyl-*N*-phenylhydrazine and this immediately decomposes to phenylhydrazine and benzoic acid.

Besides the above diphenyl derivative VI, attempts to prepare some analogues were frustrated except *ψ*-2, 4-dihydro-4-methyl-5-phenyl-2-keto-1-oxa-3, 4-diazole (IX) by the inaccessibility of *α*-acylhydrazines. The compound IX was prepared, in very poor yield, by the same treatment of *N*-benzoyl-*N*-methylhydrazine as that used for VI. Recrystallization from dry benzene afforded colorless needles, m. p. 150°C, which gave analytical figures indicative of the formula $C_9H_8O_2N_2$ (IX). Owing to the poor yield both of *N*-benzoyl-*N*-methylhydrazine and of IX, we obtained too small a quantity of IX to examine its infrared spectrum or to perform various reactions similar to those to which diphenyl derivative VI was subjected.

Experimental

***N*-Benzoyl-*N*-phenylhydrazine.**—A mixture of *N'*-acetyl-*N*-benzoyl-*N*-phenylhydrazine (5 g.), concentrated sulfuric acid (5 ml.), water (25 ml.) and ethanol (35 ml.) was refluxed for 2 hr. Silky needles which separated on cooling were filtered off, suspended in plenty of water and neutralized with sodium carbonate affording colorless prisms (3.1 g.), m. p. 66°C. Recrystallization from dilute ethanol raised m. p. to 78°C (the reported melting point is 69∼70°C.¹⁰⁾).

Found: N, 13.03. Calcd. for $C_{13}H_{12}ON_2$: N, 13.20%.

***ψ*-2, 4-Dihydro-4, 5-diphenyl-2-keto-1-oxa-3, 4-diazole (VI).**—To a solution of *N*-benzoyl-*N*-phenylhydrazine (2 g.) in chloroform (200 ml.) was added finely powdered, anhydrous potassium carbonate (20 g.) and then a violent stream of carbonyl chloride was introduced with vigorous stirring at −7°C for 10 min. After it has been kept standing overnight, reaction mixture was allowed to reflux for 30 min. and sediments were removed. The filtrate was evaporated and the residue was recrystallized from dry benzene to give colorless lancets (1.71 g.), m. p. 161∼162°C, which incorporate benzene.

Found: C, 72.16; H, 4.80; N, 10.98. Calcd. for $C_{48}H_{36}O_6N_6$ ($3\cdot C_{14}H_{10}O_2N_2$, C_6H_6): C, 72.72; H, 4.53; N, 10.66%.

When this compound was heated at 100°C under reduced pressure, benzene was removed affording white crystals, m. p. 165∼166°C.

Found: C, 70.72; H, 4.52; N, 11.62. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.58; H, 4.23; N, 11.76%.

Ethyl *N*-Benzoyl-*N*-phenylhydrazinoformate (VII).—(a) A solution of VI (0.35 g.) in absolute ethanol (10 ml.) was warmed on a water bath and after 3 hr. evaporated under reduced pressure to give white powder (0.37 g.), m. p. 132°C. Recrystallization from dilute ethanol gave colorless

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9) W. Baker and W. D. Ollis, *Quart. Rev.*, **11**, 22 (1957).

** When heated with aqueous acid, the sydnones give *N*-substituted hydrazine, carboxylic acid and carbon dioxide. The interesting production of *α*-acylhydrazine is observed only when 3-phenylsydnone is treated with one molecular proportion of water and hydrogen bromide.

10) O. Widman, *Ber.*, **26**, 947 (1893).

needles, m. p. 135~136°C, undepressed by admixture with the authentic sample prepared by route (b).

Found: C, 67.18; H, 5.92; N, 10.03. Calcd. for $C_{16}H_{16}O_3N_2$: C, 67.59; H, 5.67; N, 9.85%.

(b) To a solution of *N*-benzoyl-*N*-phenylhydrazine in ether was added equimolar ethyl chloroformate and the solid which separated was filtered off and recrystallized from dilute ethanol affording colorless needles, m. p. 136°C (Found: N, 9.95%).

Cyclohexyl *N*-Benzoyl-*N*-phenylhydrazinoformate (VIII).—A mixture of VI (0.5 g.), cyclohexanol (1 ml.) and dry benzene (20 ml.) was refluxed for 6 hr., evaporated under reduced pressure and the residue washed with ether and recrystallized twice from dilute dioxane to give colorless needles, m. p. 138~139°C.

Found: N, 8.05. Calcd. for $C_{20}H_{22}O_3N_2$: N, 8.28%.

***N*, *N'*-Di(benzanilido)urea.**—(a) *N*-Benzoyl-*N*-phenylhydrazine (1 g.) and VI (0.5 g.) were finely powdered, mixed up and kept at 100°C for 20 min. The cooled, hard solid was washed thoroughly with ether and further twice with hot chloroform (yield, 0.82 g.). Recrystallization from pyridine gave a white powder, m. p. 263°C (decomp.) (the reported melting point is 274°C[3]).

Found: C, 72.21; H, 5.33; N, 12.81. Calcd. for $C_{27}H_{22}O_3N_4$: C, 72.00; H, 4.89; N, 12.44%.

(b) VI (0.5 g.) was refluxed with water (20 ml.) with stirring for 3 hr. The precipitate was filtered off, washed with chloroform, dried (0.25 g.) and recrystallized from pyridine giving a white powder, m. p. 263.5°C (decomp.) (Found: C, 71.89; H, 4.93; N, 12.76%).

1-Benzoyl-1, 4-diphenylsemicarbazide.—VI (0.5 g.) was dissolved in purified aniline (1 ml.), heated at 100°C for 15 min. and then the solid which deposited was collected, washed with ether (yield, 0.6 g.) and recrystallized from dilute ethanol affording colorless needles, m. p. 210~211°C.

Found: C, 72.27; H, 5.37; N, 12.82. Calcd. for $C_{20}H_{17}O_2N_3$: C, 72.49; H, 5.17; N, 12.68%.

Reaction of VI with Aqueous Ammonia.—VI (1 g.) was added to concentrated aqueous ammonia (40 ml.) and stirred vigorously. After 3~4 hr. complete dissolution occurred, a pale orange color developing. After it has been kept standing at room temperature for 2 days, the reaction mixture was evaporated under reduced pressure and the residue with a smell of phenylhydrazine was collected, washed with ether, dried (yield, 0.14 g.) and recrystallized from a little water giving colorless needles, m. p. 126~127°C, undepressed by admixture with authentic benzamide.

Found: N, 11.64. Calcd. for C_7H_7ON: N, 11.57%.

Reaction of VI with Aqueous Dimethylamine.—VI (0.5 g.) was added to 40% aqueous dimethylamine (10 ml.) and stirred vigorously. After 15 min. complete dissolution occurred, an orange color developing. After it has been kept standing at room temperature for 5 days, the reaction mixture was evaporated under reduced pressure to give the residual oil which solidified on addition of concentrated hydrochloric acid. Recrystallization from ethanol-ether yielded colorless needles, m. p. 192~193°C (decomp.), which showed the positive Beilstein test.

Found: N, 11.46. Calcd. for $C_{13}H_{13}ON_2Cl$: N, 11.27%.

The authentic sample prepared by the action of concentrated hydrochloric acid on *N*-benzoyl-*N*-phenylhydrazine had m. p. 191~193°C (decomp.) (Found: N, 11.12%).

Acid Hydrolysis.—When VI (1 g.) was warmed with 10% aqueous hydrochloric acid on a water bath, complete dissolution did not occur but the form of crystallization gradually changed. The precipitate was filtered off, dried (0.66 g.) and recrystallized from water affording colorless needles, m. p. 199°C (decomp.), which showed the positive Beilstein test.

Found: C, 62.60; H, 5.49; N, 10.89. Calcd. for $C_{13}H_{13}ON_2Cl$: C, 62.78; H, 5.23; N, 11.3%.

Alkaline Hydrolysis.—VI (1 g.) was readily dissolved in 10% aqueous sodium hydroxide. After 45 min. the solution was acidified to give colorless leaflets (0.39 g.), m. p. 122°C, undepressed by admixture with authentic benzoic acid. The acidic filtrate was neutralized and extracted with ether. The extract was dried with sodium sulfate and evaporated to give an oily product, from which on addition of aqueous oxalic acid the oxalate of phenylhydrazine was obtained.

***ϕ*-2, 4-Dihydro-4-methyl-5-phenyl-2-keto-1-oxa-3,4-diazole (IX).**—To a solution of *N*-benzoyl-*N*-methylhydrazine (3.5 g.), prepared by Michaelis' method[11], in chloroform (600 ml.) was added finely powdered, anhydrous potassium carbonate (60 g.) and then a violent stream of carbonyl chloride was introduced with vigorous stirring at −5~−8°C for 10 min. After it has been kept standing overnight, the reaction mixture was refluxed for 30 min. and sediments were removed. The filtrate was evaporated to give very viscous oil with a strong smell of benzoyl chloride. Addition of ether afforded a small amount of crystalline solid, which was collected and recrystallized from dry benzene giving colorless needles, m. p. 150°C.

Found: C, 61.55; H, 4.88; N, 16.15. Calcd. for $C_9H_8O_2N_2$: C, 61.36; H, 4.58; N, 15.90%.

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[11] A. Michaelis and E. Hadanck, ibid., **41**, 3288 (1908).