acid hydrazide[13] by the procedure used for the corresponding oxadiazole.

Anal. Calcd. for $C_8H_6N_2S_2$: C, 49.5; H, 3.11; N, 14.4. Found: C, 49.5; H, 3.31; N, 14.2.

An ethanolic solution of 2-phenyl-5-mercapto-1,3,4-thiadiazole containing one equivalent of sodium ethylate was methylated with methyl iodide giving IX, m.p. 56.5–57° after crystallization from aqueous methanol. It was identical in m.p. and mixed m.p. and in infrared spectrum with IX prepared from benzyl-3-benzoyldithiocarbazate.

2-Phenyl-5-methylsulfonyl-1,3,4-thiadiazole.—A solution of 5.3 g. of IX in 300 cc. of 50% acetic acid was cooled to 10° during the 30-minute addition of chlorine gas. A solid precipitated from the solution, m.p. 130–150°, which rose to 159–160° after crystallization from ethyl acetate–petroleum ether.

Anal. Calcd. for $C_9H_8N_2O_2S_2$: C, 45.0; H, 3.36; N, 11.7. Found: C, 44.9; H, 3.30; N, 11.5.

STAMFORD, CONNECTICUT

[13] B. Holmberg, *Arkiv Kemi Mineral Geol.*, **17A**, 1 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

2-Pyrones. XII. γ-Keto-β-methylglutaconic Anhydride Arylhydrazones and Their Conversion to 1-Aryl-3-carboxy-4-methyl-6-pyridazones

BY RICHARD H. WILEY AND C. H. JARBOE, JR.[1]

RECEIVED JULY 6, 1954

Eleven aryldiazonium salts have been coupled with β-methylglutaconic anhydride to give products for which several tautomeric structures may be written. These products are intensely colored with characteristic absorption spectra. The γ-keto-β-methylglutaconic anhydride arylhydrazone structure II is indicated by ultraviolet and infrared absorption data. On hydrolysis with dilute alkali or acid, these hydrazones are converted to 1-aryl-3-carboxy-4-methyl-6-pyridazones (IV). The structure of 1-phenyl-3-carboxy-4-methyl-6-pyridazone has been established by its decarboxylation to the known 1-phenyl-4-methyl-6-pyridazone.

In previous papers, we have described[2,3] condensation reactions of β-methylglutaconic anhydride with a series of aldehydes and with several acid anhydrides. We wish to report the results of a continuing study of such reactions in which we have condensed a variety of aryldiazonium salts with this anhydride to form eleven previously uncharacterized products. There are apparently only two references in the literature reporting coupling reactions of this type. These include the reaction of benzenediazonium chloride with β-carboxyglutaconic anhydride (*trans*-aconitic anhydride)[4] and with β-chloroglutaconic anhydride.[5] The products of these reactions were assigned phenylhydrazone structures on the basis of negative ferric chloride enol tests.

The data characterizing eleven new products obtained by coupling the aryldiazonium salt with β-methylglutaconic anhydride are given in Table I. These products precipitated on adding a cold, alkaline solution of the anhydride to the diazotized amine and were recrystallized from carbon tetrachloride or ethyl acetate. Dinitroaniline was diazotized in concd. sulfuric acid and the sulfanilic acid product was precipitated at −20°. Benzidine and its 3,3′-methoxy derivative gave uncharacterizable solids. The colors varied from yellow to blue.

The ultraviolet absorption data for three of these coupling products and some related compounds are given in Table II. All three of these products are characterized by absorption maxima in the 225–240 mμ region and in the 365–400 mμ region. In addition, the phenyl and diethylaminophenyl compounds show intermediate maxima. None show a maximum at 340 mμ. Comparison of these data with the absorption data for reference compounds permits the following structural correlations. The absorption in the 225–240 mμ region is observed also with β-methylglutaconic anhydride and is attributable to the carbonyl group present in all of these compounds. The absorption in the 350–400 mμ region is characteristic of phenylhydrazones.[6] Both the wave length and intensity of the absorption band for the dinitrophenyl compound are comparable to those associated with many varieties of 2,4-dinitrophenylhydrazones. The absorption observed at 370 mμ with the unsubstituted phenyl derivative is attributable to the phenylhydrazone linkage and the absorption at 400 mμ observed with the diethylamino derivative is attributable to hydrazone absorption shifted to longer wave lengths under the influence of the diethylamino groups. The only appearance of an absorption band at frequencies characteristic of the azo linkage is that at 325 mμ (log ε 4.19) for the diethylamino derivative. However, this absorption maximum corresponds to that at 285 mμ in the curve for the unsubstituted phenyl analog, shifted to longer wave lengths under the influence of the diethylamino group. The absence of absorption at 340 mμ, as well as negative ferric chloride enol tests, is indicative of the absence of the enolic hydroxyl. Such enolic absorption is observed with β-methylglutaconic anhydride but is weak and, as with the dialkyl glutaconates,[7] does not obey Beer's law, is stronger in dilute alkali

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[1] The authors wish to acknowledge support of this research through a grant (NSF-G55) from the National Science Foundation. For the previous paper in this series see R. H. Wiley and A. N. Moyer, THIS JOURNAL, **76**, 5706 (1954).

[2] R. H. Wiley, E. L. DeYoung and N. R. Smith, *ibid.*, **76**, 1675 (1954).

[3] R. H. Wiley and N. R. Smith, *ibid.*, **74**, 3893 (1952).

[4] R. Malachowski, M. Giedroyo and Z. Jerzmanowskai, *Ber.*, **61**, 2527 (1928).

[5] R. Malachowski and T. Kalinski, *Roczniki Chem.*, **6**, 768 (1926); *C. A.*, **21**, 3615 (1927).

[6] Landolt-Börnstein, "Zahlenwerte und Functionen," Sixth edition, Vol. III, part 3, Springer Verlag, Berlin, 1951, pp. 156, 286; F. Ramirez and A. F. Kirby, THIS JOURNAL, **75**, 6026 (1953); **76**, 1037 (1954).

[7] L. Bateman and H. P. Koch, *J. Chem. Soc.*, 216 (1945).

than ethanol, and is absent in ether solutions. It is possible that such weak absorption would be obscured in these products. The absence of the enolic hydroxyl at position 6 as in formula I is further substantiated by failure of the products to form chelates under a variety of conditions. The products are, however, acidic, can be titrated as acids, and can be recovered unchanged on acidification of alkaline solutions. These data are in agreement with the phenylhydrazone structure II for these compounds in methanol with the possibility that, in base, a resonance stabilized ion can be formed by removal of a proton from I or II. Preference for salt formation in the 2-hydroxy-6-keto form corresponding to I would account for acidic properties and failure to chelate.

Infrared absorption data[8] for the phenylhydrazone (II, Ar is C_6H_5) show absorption at the carbonyl stretching frequencies, 5.7 and 5.95 μ shifted slightly from the usual positions for cyclic anhydride carbonyl, and absorption at the carbon–oxygen stretching frequency, 8.0 μ, typical of anhydrides. Although shifted, the difference between the two anhydride carbonyl absorption bands, 0.25 μ, is comparable to that in other anhydrides. There is also an absorption band at 6.25 attributable to the conjugated C—N linkage. Absorption at the N–H bending frequency, 6.5–6.6 μ, appears in measurements made with both potassium bromide and mineral oil suspensions of the compound and absorption at the 3.2 μ stretching frequency, also in both media, establishes the presence of this linkage.

Hydrolysis of the γ-keto-β-methylglutaconic anhydride arylhydrazones takes place with recyclization to give an N-arylpyridazonecarboxylic acid. The products are formed readily on basic hydrolysis and also, but less readily, with acid. The acids are colorless with no ultraviolet absorption and infrared absorption at the carbonyl stretching frequencies 5.75 μ (carboxyl carbonyl) and 6.03 μ (amide carbonyl). A similar cyclization has been reported previously in the hydrolytic conversion of a diethyl γ-ketoglutaconate phenylhydrazone to a 1-phenyl-3-carboxy-6-pyridazone.[9] Decarboxylation of 1-phenyl-3-carboxy-4-methyl-6-pyridazone (IV, Ar = C_6H_5) to the known[10] 1 phenyl-4-methyl-6-pyridazone, m.p. reported 86°, observed 84°, further confirms the assigned structures. Neither the *p*-nitrophenyl- or 2,4-dinitrophenylhydrazones undergo this hydrolytic conversion.

Experimental

γ-Keto-β-methylglutaconic Anhydride *o*-Methoxyphenylhydrazone (I, Ar = *p*-$CH_3OC_6H_4$).—A solution of 0.62 g. (0.005 mole) of *p*-anisidine in 25 ml. of water and 8 ml. of 12 *N* hydrochloric acid was cooled to 0°. A 10% aqueous solution of sodium nitrite was added until a starch–iodide test indicated an excess of nitrous acid. A solution of 0.63 g. (0.005 mole) of β-methylglutaconic anhydride in 25 ml. of water containing 0.2 g. of sodium carbonate was cooled to 0° and added slowly to the diazotized amine to precipitate the crude product. Recrystallization from carbon tetrachloride gave 0.80 g., 62% of the theoretical amount, of γ-keto-β-methylglutaconic anhydride *o*-methoxyphenylhydrazone, m.p. 222°.

The diazotization and coupling reactions were run following this same general procedure with *m*-trifluoromethylaniline, *p*-anisidine, α- and β-naphthylamine, aniline (as its hydrochloride), *p*-dimethylaminoaniline, *p*-diethylaminoaniline and *o*-nitroaniline. The 2,4-dinitroaniline was dissolved in concd. sulfuric acid and diazotized by adding solid sodium nitrite.[11] This solution was mixed, slowly and with cooling to below 5°, with the anhydride solution. The product from the diazotized sulfanilic acid was precipitated by cooling the reaction mixture to −20°. The data describing the products from these reactions are summarized in Table I.

When benzidine or 3,3′-dimethoxybenzidine was tetrazotized and coupled with β-methylglutaconic anhydride by this procedure, deep red solids were obtained which were infusible and insoluble in all solvents tested. Analytical data indicated possible addition of water to the azo compound predicted by analogy with the other coupling reactions.

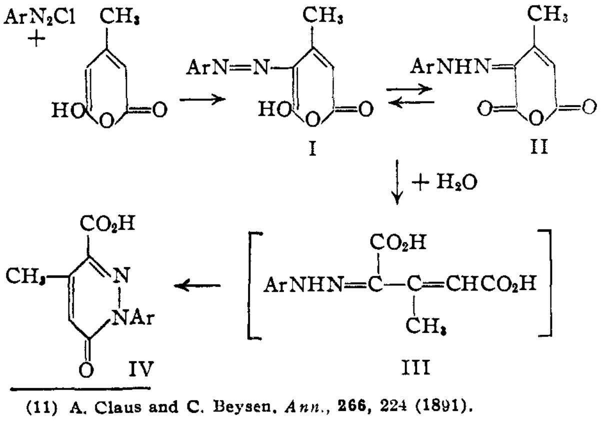
ULTRAVIOLET ABSORPTION CHARACTERISTICS OF COMPOUNDS

Compound	mμ^a
β-Methylglutaconic anhydride	225 (ϵ 2.0) E 340 (ϵ 0.6) E 230 (ϵ 1.0) N 340 (ϵ 1.46) N 230 (3.8) D
γ-Keto-β-methylglutaconic anhydride *o*-Methoxyphenylhydrazone	240 (3.66) 287 (3.55) 370 (3.89)
γ-Keto-β-methylglutaconic anhydride 2,4-Dinitrophenylhydrazone	232 (4.40) 365 (4.72)
γ-Keto-β-methylglutaconic anhydride *p*-Diethylaminophenylhydrazone	232 (4.19) 262 (4.18) 325 (4.19) 400 (3.86)
1-Phenyl-3-carboxy-4-methyl-6-pyridazone	240 (3.96) 310 (3.71)

[a] Values are for log ϵ except where noted. Measurements were made in absolute methanol except as noted; E, ethanol; N, 0.001 *M* sodium hydroxide; D, diethyl ether.

1-Phenyl-3-carboxy-4-methyl-6-pyridazone (IV, Ar = C_6H_5).—A mixture of 2.3 g. of γ-keto-β-methylglutaconic anhydride phenylhydrazone and 100 ml. of 10% aqueous potassium hydroxide was refluxed for two hours. During this time the anhydride dissolves and its color is discharged. The cooled reaction mixture is extracted with ether and acidified to precipitate the crude product as a solid. Recrystallization from boiling water gives 1.1 g., 49% of the theoretical amount, of 1-phenyl-3-carboxy-4-methyl-6-pyridazone as needles, m.p. 230° (cor.).

CHART I



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[8] The authors are indebted to Mr. Cham Cannon of the Tennessee Eastman Company for initial determination of these infrared absorption data and for helpful discussions on their interpretation.

[9] F. Heinrich, *Ann.*, **376**, 121 (1910).

[10] J. Druey, A. Huni, K. Meier, B. H. Ringier and A. Stachelin, *Helv. Chim. Acta*, **37**, 510 (1954).

[11] A. Claus and C. Beysen, *Ann.*, **266**, 224 (1891).

TABLE I

γ-KETO-β-METHYLGLUTACONIC ANHYDRIDE ARYLHYDRAZONES

Aryl group	Color	M.p., °C.	Yield, %	Re-crystd.[a] from	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Phenyl	Orange plates	175	70	C	62.60	62.66	4.38	4.60	12.17	12.38
m-Trifluoromethylphenyl	Yellow	182.3	65	C	52.40	52.47	3.04	3.12	9.40	9.53
o-Methoxyphenyl	Orange-brown needles	222	62	C	59.99	59.95	4.65	4.44	10.77	10.72
p-Methoxyphenyl	Rusty-orange needles	205	40	C	59.99	60.13	4.55	4.61	10.77	10.82
Sodium sulfophenyl	Yellow needles	>360	85	..	...	...	..	..	8.44[b]	8.50
2-Naphthyl	Red-orange needles	264	85	E	68.56	68.44	4.32	4.61	10.00	10.21
1-Naphthyl	Red-orange needles	218	85	E	68.56	68.52	4.32	4.51	10.00	10.29
p-Dimethylaminophenyl	Blue needles	211	72	E	61.53	61.73	5.53	6.37	15.38	15.34
p-Diethylaminophenyl	Blue cubes	171	71	E	63.77	63.88	6.36	6.20	13.95	14.28
o-Nitrophenyl	Orange plates	247	64	E	52.37	52.61	3.30	3.44	15.27	15.23
2,4-Dinitrophenyl	Orange-brown plates	230	69[c]	E	45.01	45.23	2.52	2.40	17.50	17.22
2,4-Dinitrophenyl	Yellow needles	230	69[c]	E	45.01	45.11	2.52	2.39	17.50	17.31

[a] C, carbon tetrachloride; E, ethyl acetate. [b] As monohydrate. *Anal.* Calcd. (as monohydrate): S, 9.64. Found: S, 9.35. [c] Combined yield of both products.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: C, 62.60; H, 4.38; neut. equiv., 230.2. Found: C, 62.42; H, 4.42; neut. equiv., 224.

1-(*o*-Methoxyphenyl)-3-carboxy-4-methyl-6-pyridazone (IV, Ar = *p*-$CH_3OC_6H_4$).—This compound was prepared by alkaline hydrolysis of 2.61 g. of γ-keto-β-methylglutaconic anhydride *o*-methoxyphenylhydrazone. There was obtained 1.4 g., 53% of the theoretical amount, of 1-(*o*-methoxyphenyl)-3-carboxy-4-methyl-6-pyridazone, m.p. 234° (cor.).

Anal. Calcd. for $C_{13}H_{12}O_4N_2$: C, 59.99; H, 4.65; N, 10.77; neut. equiv., 260.2. Found: C, 60.08; H, 4.62; N, 10.77; neut. equiv., 251.

1-Phenyl-4-methyl-6-pyridazone.—The pyridazinecarboxylic acid (2.3 g.) prepared as described above was decarboxylated by heating to 240° for five minutes. The residue was extracted with 12 *N* hydrochloric acid. The extracts were decolorized and made basic to precipitate the crude product. Additional product was obtained by ether extraction. Recrystallization from diethyl ether–petroleum ether at −20° gave 0.9 g., 50% of the theoretical amount, of 1-phenyl-4-methyl-6-pyridazone, hygroscopic needles, m.p. 84°, reported[9] m.p. 86°.

Anal. Calcd. for $C_{11}H_{10}N_2O$: N, 15.05. Found: N, 15.01.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

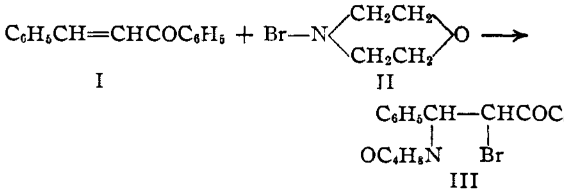
The Addition of N-Bromomorpholine to Benzalacetophenone

BY PHILIP L. SOUTHWICK AND WILLIAM L. WALSH[1]

RECEIVED JULY 22, 1954

The possibility of adding an N-haloamine to an unsaturated compound has been demonstrated; direct addition of the elements of N-bromomorpholine to *trans*-benzalacetophenone has produced a new form of α-bromo-β-morpholinobenzylacetophenone, the diastereoisomer of the previously known form. Hydrolysis and methanolysis of the new isomer proceeded readily, yielding, respectively, α-morpholino-β-hydroxybenzylacetophenone and a compound thought to be α-morpholino-β-methoxybenzylacetophenone. The stereochemical aspects of these reactions are discussed.

In the investigation to be described here it has been shown that the elements of N-bromomorpholine (II) can be added directly to the olefinic double bond of benzalacetophenone (I) to yield as the chief product a new diastereoisomeric form of α-bromo-β-morpholinobenzylacetophenone (III).[2]



I II III

$$C_6H_5CH{=}CHCOC_6H_5 + Br{-}N\begin{matrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{matrix}O \longrightarrow \begin{matrix} C_6H_5CH{-}CHCOC_6H_5 \\ \quad | \qquad\quad | \\ OC_4H_8N \quad Br \end{matrix}$$

This result establishes the possibility of N-haloamine addition to unsaturated compounds. It supports the opinion previously advanced that reactions of iodine–amine complexes with α,β-unsaturated carbonyl compounds proceed *via* an initial addition of the elements of an N-iodoamine.[3]

In benzene or ether solutions one mole of bromine reacts with one mole of morpholine with the formation of an orange precipitate which may be analogous to the iodine–morpholine complex.[3,4] However, unlike the iodine–morpholine complex, which can exist in the presence of considerable amounts of excess morpholine, the bromine–morpholine complex is immediately decomposed by the action of an additional mole of morpholine to give morpholine hydrobromide in a nearly quantitative yield. The white precipitate of morpholine hydrobromide may be filtered from the mixture to leave pale-yellow

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[1] Institute Fellow in Organic Chemistry, 1952–1953. This paper is based on a portion of the Ph.D. Thesis of William L. Walsh, Carnegie Institute of Technology, June, 1953.

[2] N. H. Cromwell, THIS JOURNAL, **62**, 2897 (1940), first described the other racemic form of this compound, which is produced by the addition of morpholine to α-bromobenzalacetophenone. Jordan, Lutz and Hinkley, ref. 7, recently showed that the same isomer is produced by the action of morpholine on either diastereoisomer of benzalacetophenone dibromide or on either geometric isomer of α-bromobenzalacetophenone.

[3] (a) P. L. Southwick, and D. R. Christman, THIS JOURNAL, **74**, 1886 (1952); (b) P. L. Southwick and D. R. Christman, *ibid.*, **75**, 629 (1953).

[4] R. V. Rice and G. D. Beal, U. S. Patent, 2,290,710 (July 21, 1943); *C. A.*, **37**, 602 (1943).