tuted.[7] The same product was obtained in each of the following runs: (a) 0.028 mole of pyridazine was added to a solution of 0.0054 mole of *trans*-1,4-dibromo-2-butene and the mixture heated to refluxing; (b) a solution of 0.059 mole of pyridazine in 100 cc. of carbon tetrachloride was added dropwise with stirring and cooling to a solution of 0.24 mole of *cis*-1,4-dibromo-2-butene; (c) a solution of 0.016 mole of pyridazine in 620 cc. of acetone was added dropwise to 0.018 mole of *cis*-1,4-dibromo-2-butene in 560 cc. of acetone at room temperature.

N-Methylpyridazinium iodide. A mixture of 5.5 g. (0.069 mole) of pyridazine and 34 g. (0.24 mole) of methyl iodide was heated in a sealed tube at 100° for 12 hr. After chilling in an ice bath, two phases were present, a dark upper phase containing yellow crystals, and a light red bottom phase of methyl iodide. The total content was added to 40 cc. of acetone, the mixture chilled in an ice bath, and filtered. The yellow prisms weighed 11.3 g. (75%) and melted with decomposition at 93–94°. Crystallization from 1-propanol gave yellow hygroscopic needles, m.p. 95–96° (dec.).

Anal. Calcd. for $C_5H_7IN_2$: C, 27.04; H, 3.18; I, 57.16; N, 12.62. Found: C, 27.3; H, 3.2; I, 56.6; N, 12.4.

Infrared spectrum, Nujol mull: maxima at 6.30, 6.88, 10.18, and 12.84 μ. The same product was obtained in the absence of solvent at 0° and in methanol solution at 110°.

N-Ethylpyridazinium bromide. A mixture of 2.21 g. (0.0028 mole) of pyridazine and 14.5 g. (0.13 mole) of ethyl bromide was heated in a sealed tube at 110° for 20 hr. On cooling an upper light yellow phase separated from a lower dark red phase of ethyl bromide. The upper phase solidified on further cooling in an ice bath. The mixture was filtered in a dry box and the solid washed with dry acetone. Crystallization from 1-propanol gave pale tan plates that melted in a sealed tube at 118–120° (dec.). The product was very hygroscopic and all transfers were made in a dry box.

Anal. Calcd. for $C_6H_9BrN_2$: C, 38.11, H, 4.80; Br, 42.27; N, 14.82. Found: C, 37.9; H, 4.8; Br, 42.0; N, 15.0.

Infrared spectrum, Nujol mull: maxima at 6.30, 8.44, 10.08, and 12.84 μ.

Department of Chemistry
Stanford University
Stanford, Calif.

---

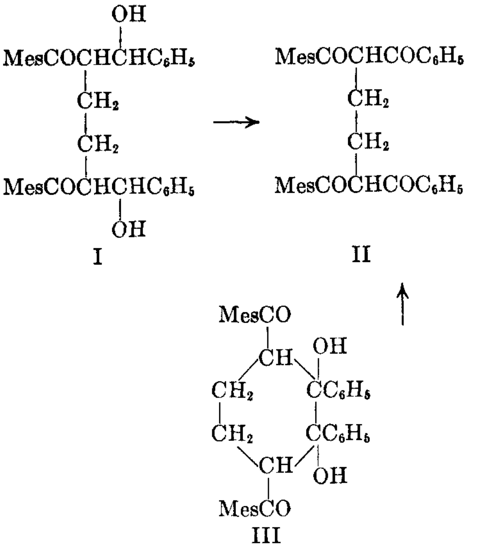
(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 34.

Isomerization of 1,4-Dibenzoyl-1,4-Dimesitoylbutane[1]

Reynold C. Fuson and H. Scott Killam

Received February 14, 1957

1,4-Dibenzoyl-1,4-dimesitoylbutane (II), prepared from the diol I by the action of chromic anhydride in glacial acetic acid, was found to melt at 201–203°.[2] The same substance was obtained by the oxidation of the cyclic glycol III by way of a compound melting at 124–126°. Evidence has now been found which indicates that this intermediate compound and that melting at 201–203° are diastereoisomers.



Repetition of the oxidation of the linear glycol I was accomplished without difficulty, but more extensive purification raised the melting point to 133°. When this material, or the less pure sample, is recrystallized repeatedly from ethanol, it is transformed into the high-melting compound (m.p. 201–203°).[3] This change can be accomplished also merely by heating the low-melting isomer in benzene. It seemed probable that the change from the low- to the high-melting isomer is an epimerization, realized by way of an enol form. As was to be expected on this basis, treatment with sodium methoxide was found to bring about the conversion. In these experiments the high-melting isomer was always obtained as a colorless powder.[3] It was observed also that this isomer could not be formed by seeding solutions of the low-melting isomer.

EXPERIMENTAL

Chromic anhydride oxidation. A solution of 1 g. of the linear glycol I was prepared by shaking it with 25 ml. of glacial acetic acid for 30 min. at room temperature. The chromic anhydride reagent, made from 1.1 g. of the anhydride, 10 ml. of glacial acetic acid, and 3 ml. of water, was added in portions over a period of 5 min. during which time the reaction mixture was swirled vigorously. The brown solution was allowed to stand at room temperature, with occasional agitation, for 2 hr.; during the latter part of this time the tetraketone II separated in the form of pale yellow needles. The product was washed on the filter, first with cold glacial acetic acid and then with cold water. The water caused the separation of a second crop of the tetraketone from the filtrate. The two crops of material were recrystallized separately from ether–petroleum ether mixtures. In each case the product formed pale yellow needles, m.p. 133–134°.[3]

Anal. Calcd. for $C_{38}H_{38}O_4$: C, 81.69; H, 6.86. Found: C, 81.74; H, 6.82.

The infrared spectrum contains absorption bands corresponding to a conjugated (1677 cm.$^{-1}$) and to an unconjugated carbonyl group (1705 cm.$^{-1}$). There is no evidence of

---

(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) R. C. Fuson and R. W. Hill, *J. Org. Chem.*, 19, 1575 (1954).

(3) R. C. Fuson and R. W. Hill, *J. Org. Chem.*, 21, 1553 (1956).

the presence of hydroxyl groups. The expected absorption for a mesityl group and a phenyl group is shown.

Isomerization was observed when the tetraketone was recrystallized repeatedly from ethanol or 1-propanol. When 0.5 g. of the compound was boiled with ethanol for a few minutes it was converted to a colorless powder which still melted at 133–134°. When the contact with boiling ethanol was prolonged, the product was a colorless powder melting at 199–200° (corr.). Under the same conditions the sample described earlier[2] was found to melt at 199–200° (corr.). A mixture of the two samples melted at 199–200° (corr.).

Anal. Calcd. for $C_{38}H_{38}O_4$: C, 81.69; H, 6.86. Found: C, 81.44; H, 7.18.

The infrared spectrum is identical to that obtained for the low-melting product.

The isomerization was accomplished also by use of sodium methoxide. The reagent was made by shaking 0.5 g. of the methoxide with 10 ml. of methanol and removal of undissolved methoxide by filtration. The reagent was added to a methanolic solution of 0.1 g. of the tetraketone (m.p. 133–134°). The solution, which immediately became pale yellow, was allowed to stand for 15 min. at room temperature. Dilute hydrochloric acid was added until a permanent turbidity was produced. The product, which separated during 2 hr. of refrigeration, crystallized from ethanol as a colorless powder melting at 199–200° (corr.). A mixture melting point with the sample described above was not depressed.

The same two tetraketones were obtained by oxidation of the cyclic glycol III with periodic acid. When the oxidation product was recrystallized from an ether–petroleum ether mixture, pale yellow crystals melting at 133–134° were obtained. When the recrystallization solvent was ethanol, however, the product separated as a colorless powder. This product and its mixture with the high-melting tetraketone from the linear glycol melted at 199–200° (corr.).

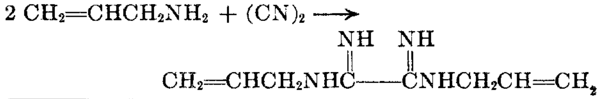
THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

Reaction of Cyanogen with Organic Compounds. IX. Allyl Amines

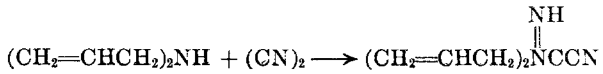
HENRY M. WOODBURN, CHEN MING CHIH,[1] AND DONALD H. THORPE[2]

Received December 6, 1956

Several years ago it was shown in this laboratory[3,4] that saturated primary and secondary aliphatic amines react with cyanogen at low temperature and atmospheric pressure to yield oxamidines and cyanoformamidines. We report here the similar behavior of the unsaturated compounds allylamine and diallyl amine:



$$2\,CH_2{=}CHCH_2NH_2 + (CN)_2 \longrightarrow CH_2{=}CHCH_2NH\overset{NH}{\overset{\|}{C}}{-}\overset{NH}{\overset{\|}{C}}NHCH_2CH{=}CH_2$$



$$(CH_2{=}CHCH_2)_2NH + (CN)_2 \longrightarrow (CH_2{=}CHCH_2)_2N\overset{NH}{\overset{\|}{C}}CN$$

These compounds are important in our current study of the chemistry of oxamidines because they possess nitrogen-free reactive centers somewhat removed from the $C{=}NH$ and $C{\equiv}N$ groups.

Physically the allyl derivatives are quite similar to their saturated analogs.[3,4] The oxamidine is a white, crystalline solid, soluble in water, ethanol, carbon tetrachloride, acetone, and ether, and insoluble in petroleum ether. It quickly turns brown in air, but forms a stable, crystalline dihydrochloride. The cyanoformamidine is a colorless liquid when freshly distilled but darkens on standing, even in the ice chest. Its hydrochloride is a stable, white solid.

The behavior of the new compounds toward bromine was investigated. From *sym*-diallyloxamidine, or better from its hydrochloride, was obtained a white, crystalline compound which gave the correct analysis for

$$CH_2BrCHBrCH_2NH\overset{NH}{\overset{\|}{C}}{-}\overset{NH}{\overset{\|}{C}}NHCH_2CHBrCH_2Br\cdot 2HCl$$

Both diallylcyanoformamidine and its hydrochloride decolorized bromine solutions readily but the gummy products could not be purified. A quantitative bromination with KBr-$KBrO_3$ solution indicated that four equivalents of bromine reacted with one mole of cyanoformamidine.

Difficulty was experienced in determining the chlorine content of *N*-diallylcyanoformamidine hydrochloride. Both Mohr and Volhard methods gave consistent results about 3% higher than theoretical. However, titration of the hydrochloride with standard sodium hydroxide gave an equivalent weight corresponding to the calculated value. It is conceivable that the cyanoformamidine forms a complex with $AgNO_3$ thus consuming part of the precipitant.

Although *sym*-diallyloxamidine can be obtained by the conventional method of cyanogenating an aqueous solution,[3] the most successful method employs petroleum ether, from which the product precipitates as formed.

EXPERIMENTAL

Cyanogen was prepared, purified and dried by the method described by Woodburn, Morehead, and Bonner.[4]

sym-Diallyloxamidine dihydrochloride. A solution of 10 g. of allylamine in 25 g. of petroleum ether was placed in an ice bath and maintained at 0° while cyanogen gas was bubbled in. After some time light-colored crystals of product appeared. Cyanogenation was discontinued soon thereafter, since experience showed that further cyanogenation converted the crystals to a brown liquid.

The crystals were filtered, dissolved in diethyl ether, and the solution saturated with dry hydrogen chloride. The precipitated hydrochloride was purified by dissolving it in ethanol and reprecipitating with ether. White crystals, melt-

---

(1) Present address: Foramino, Inc., Kenova, W. Va.

(2) Present address: Durez Plastics Division, Hooker Electrochemical Co., Walck Road, North Tonawanda, N. Y.

(3) Woodburn, Morehead, and Chen, *J. Org. Chem.*, 15, 535 (1950).

(4) Woodburn, Morehead, and Bonner, *J. Org. Chem.*, 14, 555 (1949).