uptake of hydrogen ceased. The product (64%), isolated according to the method outlined above, was obtained as a heavy white precipitate, m.p. 312–315° (dec.), which did not depress the m.p. of the sample prepared by method A. Reduction of the pyridone (I) in absolute alcohol or in glacial acetic acid, using Raney nickel as a catalyst, was not successful at either low or high pressures.

3-Carboxy-4,6-dimethyl-2-pyridol (VII). A. From I.—VII was prepared from I by acid hydrolysis by the method of Wenner and Plati,[9] in a 30% yield, m.p. 257–258°. Hydrolyses of I in more dilute acid gave VI,[10] which was identical to the product obtained by decarboxylation of VII.

B. From VIIIb.—VII was prepared from VIIIb by saponification. The product did not depress the m.p. of the sample obtained by method A.

3-Carbomethoxy-4,6-dimethyl-2-pyridol (VIIIa).—A solution of 1 g. of VII in 100 ml. of methanol containing 10 ml. of concentrated sulfuric acid was refluxed three hours. After neutralization of the acid with sodium bicarbonate, and removal of the excess methanol, the aqueous solution was extracted with ether. Removal of the organic solvent and recrystallization from ethyl acetate gave white crystals, m.p. 182–183° (50% yield). The material gave a positive ferric chloride test.

Anal. Calcd. for $C_9H_{11}NO_3$: N, 7.7. Found: N, 8.0.

2-Methoxy-3-carbomethoxy-4,6-dimethylpyridine (X).—To a cooled suspension of 1 g. of the acid (VIII) in methanol was added, with swirling, an ethereal solution of diazomethane (approximately 4.2 g.). Bubbles appeared immediately accompanied by the disappearance of the yellow color and fairly rapid solution of the acid. After standing for 24 hours, the solution was distilled to dryness leaving a yellow oil. An ethereal solution of this was washed with sodium bicarbonate solution and then with water. The ethereal solution was then dried over potassium carbonate and distilled. The residue was vacuum sublimed to give a colorless solid, m.p. 57–58° (56% yield).

Anal. Calcd. for $C_{10}H_{13}NO_3$: N, 7.2. Found: N, 7.4.

The solubility of X in ether rules out any possible zwitterion structure. The low melting point and the marked ability of the compound to sublime are consistent with the α-methoxy structure.

3-Hydroxymethyl-4,6-dimethyl-2-pyridol (IX).—Two grams of ethyl ester (VIIIb) were placed in a Soxhlet extractor above a refluxing solution of 4 g. of lithium aluminum hydride in 150 ml. of anhydrous ether. Refluxing was continued until all the ester had been carried down into the ether solution (24 hours). The solution was then allowed to stand overnight and then 15 ml. of methanol followed by 15 ml. of water were added dropwise through the condenser. The suspension was filtered and the precipitate thoroughly extracted with several portions of methanol. The methanol solution was then saturated with carbon dioxide and the solvent removed under reduced pressure. The residue was then taken up in hot 95% ethanol. Removal of the ethanol at reduced pressure left a white residue which was recrystallized from ethyl acetate containing a little ethanol. The product, m.p. 211–212° (60% yield), gave a positive ferric chloride test.

Anal. Calcd. for $C_8H_{11}NO_2$: N, 9.1. Found: N, 9.2.

The picrate melted at 124.5–125.5°.

Anal. Calcd. for $C_{14}H_{14}N_4O_9$: N, 14.6. Found: N, 14.6.

The hydrochloride of IX was a very hygroscopic substance.

Diazotization Experiments.—The following attempts to convert the β-aminomethyl group into a β-hydroxymethyl group were carried out without success. (A) IV was treated with sodium nitrite in (a) hot *M* sulfuric acid, (b) in hot 4 *M* hydrochloric acid, (c) in cold 0.8 *M* acetic acid and (d) in cold acetic acid solution buffered to *p*H of 5 with sodium acetate. (B) V was treated with sodium nitrite in (a) 3.3 *M* cold acetic acid, and (b) in cold acetic acid solution buffered to *p*H of 5 with sodium acetate and in the presence of hydroquinone.

Evanston, Ill. Received November 24, 1950

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[9] W. Wenner and J. T. Plati, *J. Org. Chem.*, **11**, 751 (1946).

[10] J. C. Bardhan, *J. Chem. Soc.*, 2223 (1929).

[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Azo-bis-nitriles. III.[1] The Preparation and Decomposition of Azo-nitriles. Steric Factors

By C. G. Overberger and M. B. Berenbaum

This work was undertaken to prepare both the *meso-* and DL-forms of several aliphatic azo compounds in order to measure their rates of decomposition to test previous predictions. (1) The preparation of 1,2-disubstituted hydrazines of the type $CH_3R(CN)C{-}NH{-}NH{-}C(CN)RCH_3$ from sterically hindered ketones by the addition of hydrogen cyanide to the corresponding azine is described. (2) The preparation and characterization of the *meso-* and DL-forms of the azo compounds of the type $CH_3R(CN)C{-}N{=}N{-}C(CN)RCH_3$ where $R{=}(CH_3)_2CH{-}CH_2{-}$, cyclo-$C_3H_5{-}$ and $(CH_3)_3C{-}$ is described. (3) The rate of decomposition for the isomeric azo compounds have been determined. In no case, is there an appreciable difference in the rate of decomposition of the isomers in toluene at the same temperature. (4) Accurate activation energies for these decompositions have been determined. (5) Differences in decomposition rate of the various azo compounds are attributed to steric and resonance factors.

In a previous paper,[2a] the preparation and decomposition of some aliphatic azo nitriles were reported. Differences in decomposition rates were attributed to steric factors. We have now extended several phases of this work. This paper will describe the preparation, separation and decomposition of two stereoisomeric forms (probably the *meso-* and *dl*-forms of the *trans*-azo configuration) of the azo compounds derived from methyl cyclopropyl ketone, methyl isobutyl ketone and pinacolone, and the extension of a new procedure of Alderson and Robertson[3] for the preparation of azo-bis-nitriles from hindered ketones.

(A) Preparation of Azo Compounds

I. Discussion.—The isomeric azo compounds from methyl cyclopropyl ketone were prepared as described previously.[2a] This azo compound has also been reported recently by Pinkney,[4] prepared in a similar way. His product appears to be a mixture of isomers and the analysis reported is subject to some question.

The 1,2-disubstituted hydrazine from methyl isobutyl ketone (prepared previously by another method[2a]), and that from pinacolone, were prepared

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[1] This work was supported by a grant from the Research Corporation. For the second paper in this series, see C. G. Overberger, P. Fram and T. Alfrey, Jr., *J. Polymer Sci.*, in press.

[2] (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, This Journal, **71**, 2661 (1949); (b) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

[3] W. L. Alderson and J. A. Robertson, U. S. Patent 2,469,358, May 10, 1949.

[4] P. S. Pinkney, U. S. Patent 2,492,763, December 27, 1949.

according to a modification of a recent patent.[3] The azine is first prepared and then treated with liquid hydrogen cyanide at room temperature at atmospheric pressures.

$$R(R')C{=}N{-}N{=}C(R)R' \xrightarrow{HCN} R(R')C(CN){-}NH{-}NH{-}C(CN)(R)R'$$

Alderson and Robertson[3] also reported the preparation of a stereoisomeric mixture of the 1,2-disubstituted hydrazine from methyl isobutyl ketone by the above process. We have prepared the stereoisomeric hydrazines from pinacolone by the procedure of reference 3 (see Experimental section).

A procedure developed by us before publication of the above patent consisted of the simultaneous addition of anhydrous hydrazine and liquid hydrogen cyanide to the ketone. This procedure was unsuccessful with a hindered ketone such as pinacolone, but was moderately successful with methyl isobutyl ketone.[5] Presumably the azine is first formed, followed by addition of the hydrogen cyanide.

Modifications employed in the oxidation of the substituted hydrazines are described in the experimental section.

II. Experimental[6]

Preparation of 2,2'-Azo-bis-2-cyclopropylpropionitrile.—The stereoisomeric 1,2-disubstituted hydrazines from methylcyclopropyl ketone were prepared by the procedure of Thiele and Heuser.[7,2a] From 41 g. (0.49 mole) of methyl cyclopropyl ketone,[8] 16 g. (30%) of product melting at 96.5–98.0° was obtained after recrystallization of the crude product from an ether–low boiling petroleum ether mixture (94–95°, 36%).[2a]

A considerable amount of yellow-orange oil remained after evaporation of the solvent from the original mother liquor. The second hydrazine isomer could not be obtained in a pure form from this residual crude material. The oil was therefore converted directly to the corresponding azo compound by preparation of the hydrobromide and oxidation of the latter in ethanol by the method of reference 2a. After several recrystallizations of the resulting azo-nitrile from an ether–low boiling petroleum ether mixture, 9 g. (17% based on starting ketone) of crystalline product was obtained; m.p. 76–77° dec. (77–78°[2a]) (50–55°, 46% based on ketone, analysis questionable).[4]

The second isomer of the azo-nitrile was obtained from the crystalline hydrazine by the procedure of Thiele and Heuser.[7] Eleven grams (0.05 mole) of the finely powdered crystalline hydrazine was oxidized, yielding 7.3 g. (67%) of product melting at 64–64.5° dec., after recrystallization from an ether–low boiling petroleum ether mixture.

Anal.[9] Calcd. for $C_{12}H_{16}N_4$: C, 66.63; H, 7.46; N, 25.90. Found: C, 66.80; H, 7.44; N, 25.67.

Preparation of 2,2'-Azo-bis-2,4-dimethylvaleronitrile.—The hydrazines from methyl isobutyl ketone were prepared by a new technique because of the low yields obtained with the original method.[2a] A solution of 50 g. (0.50 mole) of methyl isobutyl ketone, 60 g. (2.2 moles) of liquid hydrogen cyanide and 8.0 g. (0.25 mole) of anhydrous hydrazine in 75 ml. of absolute alcohol was allowed to stand for four days at room temperature. After removal of excess hydrogen cyanide and solvent under vacuum, the residual crude semi-solid was recrystallized from an ether–low boiling petroleum ether mixture to give 20 g. (32%) of flat plates, m.p. 93–95°. Further recrystallization raised the melting point to 95.5–97° (95–96°, 11%)[2a] (95°, no yield reported except for isomeric mixture, 93%).[3]

Since the isomeric hydrazine could not be recovered in a pure form from the mother liquor from the above preparation, the hydrobromide was prepared and oxidized as described for the hydrobromide of the 1,2-disubstituted hydrazine from methyl cyclopropyl ketone. After repeated fractional recrystallization from an ether–low boiling petroleum ether mixture, the yield of azo-nitrile was 9.5 g. (15% based on starting ketone), m.p. 75–76°, dec. (74–76°)[2a] (78°, no yield, analysis uncertain).[3]

The second azo-nitrile isomer was prepared from the crystalline hydrazine by a modified oxidation procedure. A well-stirred suspension of 21.0 g. (0.084 mole) of powdered crystalline hydrazine in 80 ml. of 90% ethanol and 40 ml. of concentrated hydrochloric acid was cooled to 5–10° and the theoretical amount of bromine in 50% ethanol added slowly. The product was worked up in the usual fashion to yield 15.0 g. (72%) of flat plates melting at 56–57°, dec., after recrystallization from an ether–petroleum ether mixture (49–51°, no yield, analysis uncertain).[3]

Anal. Calcd. for $C_{14}H_{24}N_4$: C, 67.69; H, 9.74; N, 22.56. Found: C, 67.77; H, 9.94; N, 22.72.

Subsequent to utilization of the above procedure, a similar process was reported by Alderson and Robertson.[3] In their patent, liquid hydrogen cyanide is added to the previously prepared azine, generally at elevated temperature and pressure, in a medium containing less than 10% water based on the cyanide present. We have used a modification of this procedure also, to prepare the hydrazines from methyl isobutyl ketone.

A mixture of 40 g. (0.40 mole) of methyl isobutyl ketone and 10.0 g. (0.20 mole) of 100% hydrazine hydrate was refluxed for four days. After separation of the aqueous layer, the product was distilled to yield 36.5 g. (93%) of the ketazine as an almost colorless oil, b.p. 101–103° at 16 mm. (176° at atmospheric pressure),[10] $n^{25}\text{D}$ 1.4538, $d^{25}{}_4$ 0.8315.

Anal. Calcd. for $C_{12}H_{24}N_2$: N, 14.28. Found: N, 14.41.

The ketazine (36.0 g., 0.18 mole) was treated with 21 g. (0.7 mole) of hydrogen cyanide at room temperature for 24 hours. The reaction mixture was poured into water and the waxy precipitate collected by filtration. Recrystallization from ether–petroleum ether yielded 19 g. (41%) of product melting at 91.5–94°. The mother liquor contained considerable amounts of low melting material which could not be purified to give a product of constant melting point.

Preparation of 2,2'-Azo-bis-2,3,3-trimethylbutyronitrile.—Since direct reaction of pinacolone with anhydrous hydrazine and hydrogen cyanide failed to yield the desired hydrazines, a modified procedure similar to that of Alderson and Robertson[3] was used.

Pinacolone ketazine was prepared in 88% yield as described above for methyl isobutyl ketone; b.p. 87.5–88.0° at 9 mm. [b.p. 103° (17 mm.)],[11] $n^{25}\text{D}$ 1.4540, $d^{25}{}_4$ 0.8405.

Anal. Calcd. for $C_{12}H_{24}N_2$: N, 14.28. Found: N, 14.17.

A solution of 85 g. (0.43 mole) of the ketazine and 115 ml. (*ca.* 3.2 moles) of liquid hydrogen cyanide were allowed to stand for three days at room temperature. The excess hydrogen cyanide was then removed under vacuum leaving the crude mixture of hydrazines in almost quantitative yield. After tedious fractional crystallizations from ether and ether–petroleum ether mixtures, the two isomers were separated to give 65.8 g. (61%) of long prisms, m.p. 134–137°, and 19.1 g. (18%) of granular crystals, m.p. 124–126° (yield, 38%, no m.p. reported, no analysis).[3] Further recrystallization of the higher melting isomer from ether raised the melting point to 136.8–137.5°.

Anal. Calcd. for $C_{14}H_{26}N_4$: N, 22.40. Found: N, 22.15.

The melting point of the second isomer was raised to 125.5–126.8° by further recrystallization from ether. A mixture of the two isomers melted at 111–118°.

Anal. Calcd. for $C_{14}H_{26}N_4$: N, 22.40. Found: N, 22.72.

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[5] The procedure previously reported[2a] gives poor yields with methyl isobutyl ketone and other hindered ketones. Some of our work was completed prior to the appearance of the above patent[3] in "Chemical Abstracts."

[6] All melting points are corrected.

[7] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[8] Obtained through the courtesy of Mr. Johnson of U. S. Industrial Chemicals, Inc.

[9] Analyses by Mr. H. S. Clark, Urbana, Illinois; Mr. Harry Biletch and Mr. Pao-tung Huang, Polytechnic Institute of Brooklyn; Drs. Weiler and Strauss, Oxford, England; Dr. K. Ritter, Zurich, Switzerland.

[10] A. Mailhe, *Bull. soc. chim. Belg.*, [4] **29**, 219 (1921).

[11] W. Baird and F. J. Wilson, *J. Chem. Soc.*, 2116 (1927).

The azo compounds were prepared by the modified oxidation procedure used for 2,2′-azo-bis-2,4-dimethylvaleronitrile (56–57° isomer). Because of the abnormally slow rate of oxidation, the reaction mixture was allowed to stand for 72 hours at 0–5° before the product was isolated.

From the hydrazine isomer melting at 136.8–137.5°, the corresponding azo compound, melting at 110.5–113°, was obtained in 95% yield. Further recrystallization from ether raised the melting point of the plate-like crystals to 114–116° dec. (94–96°, no yield, no analysis).[8]

Anal. Calcd. for $C_{14}H_{24}N_4$: C, 67.69; H, 9.74; N, 22.56. Found: C, 67.42; H, 9.54; N, 22.55.

From the hydrazine isomer melting at 125.5–126.8°, the azo compound, melting at 113–116°, was obtained in 78% yield. Further recrystallization from ether raised the melting point of the needle crystals to 116–118° with dec.

Anal. Calcd. for $C_{14}H_{24}N_4$: C, 67.69; H, 9.74; N, 22.56. Found: C, 67.89; H, 9.46; N, 22.28.

A mixture of the two azo compounds melted at 112.5–114° dec. The differences of crystal form and the improbability of isomerization during oxidation of the substituted hydrazo compounds support the view that these compounds are isomeric despite the closeness of their melting points. They differ also in rates of decomposition, as will be seen below.

The possibility that the two forms isolated are simply different crystalline forms of the same molecular species in all cases seems remote because of the many fractional recrystallizations. In the case of the azo compounds from pinacolone, a test by cross-seeding of solutions indicated that this is not the case.

(B) Kinetic Measurements

I. Procedure.—The procedure for measuring rates of decomposition was essentially that described by Overberger, O'Shaughnessy and Shalit[2a] as modified by the inclusion of an internal magnetic stirrer and control of the bath temperature to ±0.05°.

II. Results.—The rates of decomposition of the compounds $R(CH_3)(CN)C-N{=}N-C(CN)(CH_3)-R$, where R = cyclopropyl (two isomers), isobutyl (two isomers), and *t*-butyl (two isomers) as measured by nitrogen evolution, are reported in Table I. Table I contains values of the rate of the decomposition in toluene at the specified temperature, average rate constants for each compound and energies of activation calculated from these constants and the approximate rate constant calculated for 80.2°. In Fig. 1, plots of $\ln V_\infty/V_\infty - V_t$ *vs.* time are reproduced for the decomposition of two stereoisomers derived from methyl cyclopropyl ketone at three temperatures and are examples of the general accuracy of the determination.

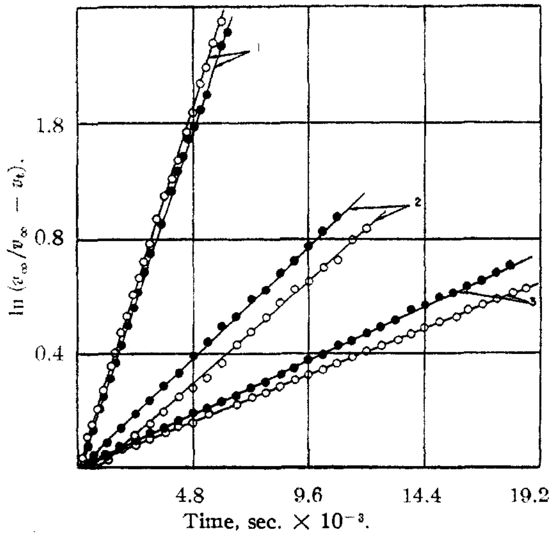

Fig. 1.—Decomposition of stereoisomeric azo-nitriles from methyl cyclopropyl ketone in toluene: (1) temperature, 59.2°; (2) temperature, 49.5°; (3) temperature, 44.2°: ●, high melting isomer (76–77°); ○, low melting isomer (64–65°).

Table I

Decomposition Rates of Azo Nitrile Stereoisomers in Toluene

$(R)(CH_3)(CN)C-N{=}N-C(CN)(CH_3)(R)$

R	Azo-nitrile m.p., °C.	k(sec.$^{-1}$ × 10^4)	Temp., °C.	No. of runs	Energy of activation, kcal./mole	k^a(sec.$^{-1}$ × 10^4) corrected to 80.2°
Cyclo-C_3H_5	64–65	0.350 ± 0.011	44.2	2	28 ± 1.0	33
		0.753 ± 0.005	49.5	2		
		2.68 ± 0.06	59.2	3		
	76–77	0.390 ± 0.05	44.2	2	26 ± 1.0	25
		0.817	49.5	1		
		2.46 ± 0.02	59.3	2		
Iso-C_4H_9	56–57	0.805	59.7	1	29 ± 2.0	10
		2.89	69.9	1		
	74–76	1.98	69.8	1	29 ± 2.0	7.1
		7.1 ± 0.0	80.2	2		
t-C_4H_9	114–116	0.688	79.5	1	35 ± 1.0	0.77
		0.742	79.9	1		
		2.59 ± 0.06	89.0	2		
	116–118	1.053 ± 0.010	79.9	2	30 ± 2.0	1.09
		3.09 ± 0.09	88.9	2		

[a] For comparisons of rates of decomposition, values of the rate constant at 80.2° have been calculated from those at the nearest experimental temperature using the experimental activation energies.

III. Discussion of Results.—These results conclusively demonstrate that there is little difference in the rates of decomposition of the stereoisomers of the three azo compounds studied (Table I). Consideration of Fisher–Hirschfelder molecular models on the basis of the steric explanation described in reference 2a, predicts this result.[12] There is considerable mutual interference of pairs of groups R and methyl, especially when R = isobutyl, at the two ends of the molecule. However, the change in configuration of one of the carbons attached to the azo group does not change this interference to any appreciable extent. Models indicate that free rotation around the carbon–nitrogen bond in the isobutyl compound is somewhat restricted by the interaction of the two ends of the molecule with each other. This interference is not present when R = *n*-butyl since the butyl group can fold back to prevent much interaction.

Previous experiments indicated that when branching occurred in the α-position of R, as in the case R = isopropyl, there was little change in the rate constant when compared with R = methyl. However, branching in the β-position, for example when R = isobutyl, resulted in an increased rate of decomposition. Models indicated that an additional methyl group in the α-position (R = *t*-butyl) would not lead to any additional strain of the type described above and this was substantiated on determination of the rate of decomposition.

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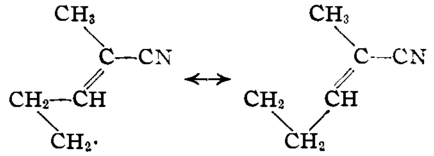
[12] Models indicate the *cis* configuration of the azo compounds is very unlikely. The two forms referred to in this paper are based on the likely assumption that only the *trans* configuration of the azo group is possible. Evidence from X-ray diffraction has substantiated this assumption in the case of 2,2′-azo-bis-isobutyronitrile.

This is a clear indication that the increase in rate when R = isobutyl is not due to "B" strain[13] since models indicate that "B" strain should be increased considerably on going from R = isobutyl to R = *t*-butyl. From Table I it can be seen that the decomposition of the azo compound derived from R = *t*-butyl is slightly slower than that derived from R = methyl[2a] at 80.2°. Both of these rates are much smaller than that of the azo compound when R = isobutyl.

The azo compound derived from methyl cyclopropyl ketone decomposes much more rapidly than either of the two other azo compounds described in this paper or any previously reported.[2a] A steric explanation of the type discussed above is not adequate or satisfactory. Semi-accurate models (it is impossible to construct a cyclopropane ring with Fisher–Hirschfelder models) indicate some crowding of the groups around each carbon due to the rigidity of the cyclopropyl group. This crowding is not present when R = isopropyl, because of the fact that the methyl groups can easily fold back. Thus, there may be an increased tendency for the cyclopropyl group to release a slight "B" strain[13] by forming the planar radical. A second explanation may be due to the increased possibilities for hyperconjugation in a cyclopropyl group contributing to increased resonance in the radical formed on decomposition. Thus, the following resonance forms can be written, in addition to those involving resonance through the nitrile group:



Klotz[14] in a study of the ultraviolet absorption spectra of compounds containing the cyclopropyl group conjugated with an olefinic or carbonyl double bond found that these compounds absorb light at longer wave lengths than the corresponding non-cyclic compounds. Similar results have been obtained by Rogers with cyclopropylbenzene and by Mariella, Peterson and Ferris[15] with 2-cyclopropylpyridine. This shift in absorption has been attributed to hyperconjugation of the three-membered ring with the double bond involving ionic resonance forms.

A discussion of errors arising from this type of measurement was included in reference 2a. For the most part, induction periods have been eliminated by careful exclusion of oxygen by nitrogen. In addition, temperature control has been improved.

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[13] H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[14] I. M. Klotz, *ibid.*, **66**, 88 (1944).

[15] M. T. Rogers, *ibid.*, **69**, 2544 (1947); R. P. Mariella, L. F. S. Peterson and R. C. Ferris, *ibid.*, **70**, 1474 (1948); see also J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950), who have suggested that the abnormally high rate of solvolysis of cyclopropol carbinyl chloride is due to stabilization of the cyclopropyl carbinyl cation by hyperconjugation involving the cyclopropane ring.

BROOKLYN, N. Y. RECEIVED NOVEMBER 14, 1950

[CONTRIBUTION FROM THE ENZYME RESEARCH DIVISION, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Bitter Principles of Citrus. II. Relation of Nomilin and Obacunone[1]

BY OLIVER H. EMERSON

Obacunone was isolated from Florida citrus seed oil, along with limonin and nomilin. Nomilic acid, previously prepared from nomilin, is identical with obacunoic acid. Nomilin is probably an acetoxy-dihydroöbacunone, with the acetoxy group in *β*-position to the carbonyl of one of the lactone groups.

Limonin, $C_{26}H_{30}O_8$, has been shown to be the bitter principle that develops on standing in the expressed juice of navel oranges.[2a,b] A similar compound, nomilin, $C_{28}H_{34}O_9$, likewise of bitter taste, occurs with limonin in the seeds of oranges and lemons. Since citrus seeds are among the best practical sources of limonin, it was hoped that the oil expressed from mixed citrus seeds, which is a commercial product of Florida, would prove an advantageous source for the preparation of large amounts of limonin. Although the bitter substances could be readily extracted from the oil, the yield of limonin was disappointing, as the chief bitter material proved to be nomilin. A third beautifully crystalline substance whose analysis indicated it to have the composition $C_{26}H_{30}O_7$ was also obtained. Although not bitter, its close relationship to nomilin was shown by the fact that hydrolysis with dilute aqueous alkali converts both substances to the same $C_{26}H_{32}O_8$ acid. The data in Table I show that this third substance is identical with obacunone isolated by Kaku and Ri[3] from the bark of *Phellodendron amurense*, and very probably also with casimirolid, obtained by Power and Callan[4] from the seeds of *Casimiroa edulis*. It is of interest that Phellodendron and Casimiroa belong to the same family (*Rutaceae*) as does Citrus, and that Kaku and Ri[3] found obacunone to occur with limonin.

The slight difference assigned by Power and Callan[4] to the composition of their product could easily be explained by difficulties in combustion, since many complex natural products are notoriously hard to burn in macro-determinations. The English workers prepared their methyl ester by treating the acid with methanolic hydrogen chloride, but the precise conditions were not stated

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[1] Enzyme Research Division Contribution No. 132. Article not copyrighted.

[2] (a) O. H. Emerson, THIS JOURNAL, **70**, 545 (1948); (b) O. H. Emerson, *Food Technology*, **3**, 248 (1949).

[3] T. Kaku and H. Ri, *J. Pharm. Soc. Japan*, **55**, 222 (1935), *C. A.*, **31**, 6643 (1937).

[4] F. B. Power and T. Callan, *J. Chem. Soc.*, **99**, 2004 (1911).