with two 150-ml. portions of ether. The original yellow solution and the ether extracts were dried over sodium carbonate and then distilled through a 75-cm. Podbielniak column to yield 11.75 g. of the diene, b.p. 68° (83 mm.), $n^{23}D$ 1.4871, d^{20}_4 0.9312; lit.[22] b.p. 37° (20 mm.).

In ethanol the diene showed absorption, λ_{max} in mμ (log ε) at 207 (3.34), 217 (3.02) shoulder, 223 (2.78) shoulder, 230–243 (2.19) broad step-out. In the vapor the diene showed some 22 sharp bonds between 223 and 200 mμ. The most intense of these lay at 213 mμ.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.54; H, 8.45.

The ultraviolet spectra were determined on a Cary recording spectrophotometer, model 14, using spectral grade solvents.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

The Wolff–Kishner Reaction with α-Oximinoketones[1]

BY HENRY RAPOPORT AND WILLIAM NILSSON[2]

RECEIVED MAY 22, 1961

The Wolff–Kishner reaction with a number of α-oximinoketones, both cyclic and acyclic, has been investigated. With the acyclic compounds, the major product is normal reduction to the corresponding oxime. However, with the cyclic compounds, both normal reduction to the oxime and *v*-triazole formation may occur, the proportion depending on steric factors. A mechanism for triazole formation has been proposed, based on the observation that substituted hydrazones do not give this reaction.

In a previous communication[3] the Wolff–Kishner reaction with α-oximinoketones was reported to yield various types of products depending on the starting material used. Thus, from 2,3-octanedione-3-oxime, a 90% yield of the normal Wolff–Kishner reduction product, 3-octanone oxime, was obtained, while biacetyl monoxime was reported to yield 2,3-butanedione hydrazone oxime. A 70% yield of phenylacetic acid was obtained from α-oximinoacetophenone, and, most interestingly of all, indano[1,2-d]-*v*-triazole was obtained from 1,2-indandione-2-oxime.

A more complete study of this reaction was of interest. In particular, it was desirable to be able to predict the probable product of the Wolff–Kishner reaction with a given α-oximinoketone from structural considerations. Contained within this general question is the more specific one of which α-oximinoketones can be expected to yield triazoles. Furthermore, it was of interest to determine the mechanism of triazole formation under Wolff–Kishner conditions, since this is a new and perhaps convenient method of triazole synthesis.

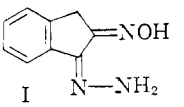
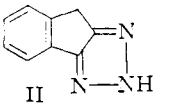
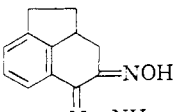
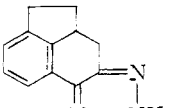
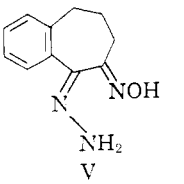
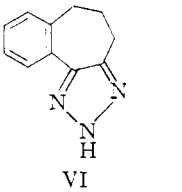
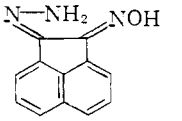
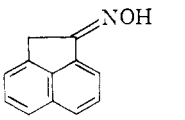
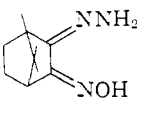
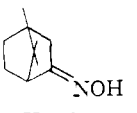
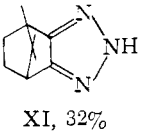
For this purpose we have, in the present work, employed a series of representative cyclic and acyclic, aliphatic and aromatic α-oximinoketones. The reaction conditions employed were, in general, those of the modified Wolff–Kishner reaction[4] except that the intermediate hydrazones of the α-oximinoketones were isolated and characterized. The hydrazone oxime then was heated at 170–190° for three hours in diethylene glycol containing potassium hydroxide, and the products were separated into neutral, acidic and alkaline fractions.

Results

The results obtained with five cyclic oximinoketones are presented in Table I. In four of the five cases, triazole formation resulted. However, the yield of triazole significantly decreases as the size of the ketone ring increases from five- to six- to seven-membered, that is as the rings become more flexible and the hydrazone and oxime groups less co-planar.

TABLE I

WOLFF–KISHNER REACTION WITH CYCLIC α-OXIMINO-KETONES

Reactant	Products	Yield, %
 I	 II	52
 III	 IV	34
 V	 VI	15
 VII	 VIII	32
 IX	 X 58%	 XI, 32%

The electronic effect of the fused aromatic ring does not appear to play a role in triazole formation since a significant yield of triazole is obtained

(1) Sponsored, in part, by the United States Atomic Energy Commission.

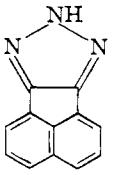
(2) National Science Foundation Predoctoral Fellow, 1958–1960.

(3) H. Rapoport and H. H. Chen, *J. Org. Chem.*, **25**, 313 (1960).

(4) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

from the purely alicyclic camphorquinone 2-hydrazone 3-oxime (IX). This is accompanied by epicamphor oxime, the normal Wolff–Kishner reduction product. Since the epicamphor oxime X is easily separated from the camphanotriazole XI this reaction can serve as a way of converting camphor to epicamphor.

It should also be noted that triazole formation does not take place if steric factors are unfavorable, as in the case of acenaphthenequinone oxime hydrazone (VII). Although the hydrazone and oxime groups are co-planar, the corresponding triazole XII could be formed only at the expense of considerable strain in the transition state and, therefore, only the competing normal Wolff–Kishner reduction to the oxime VIII takes place. From the reaction with 2-oximino-1-tetralone, no identifiable products could be isolated.

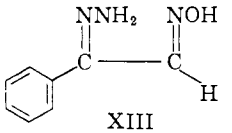
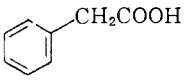
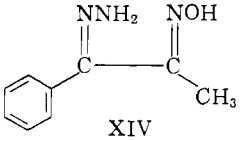
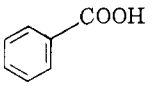
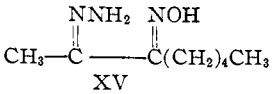
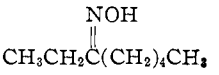
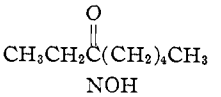
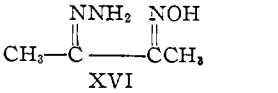
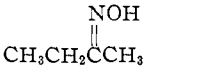


XII

Two purely aliphatic and two aryl substituted aliphatic α-oximinoketones were investigated, the results appearing in Table II. It is evident that no triazole formation takes place when the reactant is an acyclic α-oximinoketone hydrazone. Since the two functional groups are reasonably free to take opposed positions, the steric factors favoring triazole formation are absent, and this reaction does not compete with the normal Wolff–Kishner reduction in the case of both 2,3-octanedione 2-hydrazone 3-oxime (XV) and biacetyl hydrazone oxime (XVI).

TABLE II

WOLFF–KISHNER REACTION WITH ACYLIC α-OXIMINOKETONES

Reactant	Products	Yield, %
 XIII		78
 XIV		5
 XV		50
		21
 XVI		53

The conversion of α-oximinoacetophenone hydrazone (XIII) to phenylacetic acid in high yield is also explained on the basis of normal Wolff–Kishner reduction. The corresponding triazole, 4-phenyl-*v*-triazole, was synthesized independently from phenylacetylene and hydrazoic acid. This triazole was subjected to the reaction conditions and found to be completely stable. After four hours, it was quantitatively recovered unchanged; thus, 4-phenyl-*v*-triazole cannot be an intermediate in phenylacetic acid formation. On the other hand, the normal Wolff–Kishner reduction product, phenylacetaldoxime, under Wolff–Kishner conditions was converted to phenylacetic acid in about the same yield as that obtained from XIII. The ready conversion of aldehyde oximes to the corresponding acids by the action of hot alkali has been found to be quite general and will be the subject of a subsequent publication.

Finally, α-oximinopropiophenone hydrazone (XIV) was found to yield a small amount of benzoic acid as the only isolable product. Since normal Wolff–Kishner reduction of XIV to phenylacetone oxime (XVII) was suspected, the stability of the latter under the given conditions was tested. Phenylacetone oxime was found to be completely unstable when subjected to Wolff–Kishner conditions, yielding some benzoic acid and mostly non-volatile material with the same infrared spectrum as that from XIV.

Thus, it can be stated that open-chain, acyclic α-oximinoketone hydrazones invariably undergo normal Wolff–Kishner reduction to the corresponding oximes which may or may not be stable under the given reaction conditions. In some cases, the reaction may serve as a means of moving a carbonyl function to an adjacent carbon.

The ultraviolet and infrared spectra of the four new triazoles synthesized in the present work are summarized in Table III.

TABLE III

SPECTRA OF SOME *v*-TRIAZOLES

Compound	Ultraviolet absorption λ_{max}, mμ (ε) in CH_3OH	Infrared absorption λ_{max}, μ, in KBr Triazole ring vibrations
XI	228 (3,800)	8.83–8.88
		10.25–10.31
II	258 (17,200)	8.93–8.98
	264 (16,700)	10.23
	283 (6,600)	
	291 (6,300)	
IV	259 (12,700)	9.21
	267 (13,000)	10.08
	285 (5,300)	
	294(4,900)	
VI	254 (13,600)	8.95
		10.09

v-Triazole has been reported[5] to have a single absorption maximum in the ultraviolet at 210 mμ (ε 4000) and 4-alkyl-*v*-triazoles to absorb at 216 mμ (ε 5000). Since camphano[2,3-d]-*v*-triazole is a 4,5-disubstituted derivative, it would be expected to have a single maximum bathochromically displaced from that of the 4-alkyl-*v*-triazoles, as it has.

(5) L. W. Hartzel and F. R. Benson, *J. Am. Chem. Soc.*, **76**, 667 (1954).

The same authors[5] report 4-phenyl-*v*-triazole to have a single maximum at 245 mμ (ε 16,000) and a minimum at 218 mμ. Since II, IV and VI are all 4-phenyl-*v*-triazoles with an alkyl substituent at position 5, they should have similar spectra but bathochromically displaced from that of 4-phenyl-*v*-triazole. Such is the case with VI which has λ_{max} 254 mμ (ε 13,600) and λ_{min} 224 mμ. The compounds II and IV show similar absorption except that the main maximum is broken into two bands with a shallow minimum between them, and some fine structure appears at longer wave lengths. The disappearance of fine structure in the spectrum of VI may indicate some strain in this ring system (see Fig. 1).

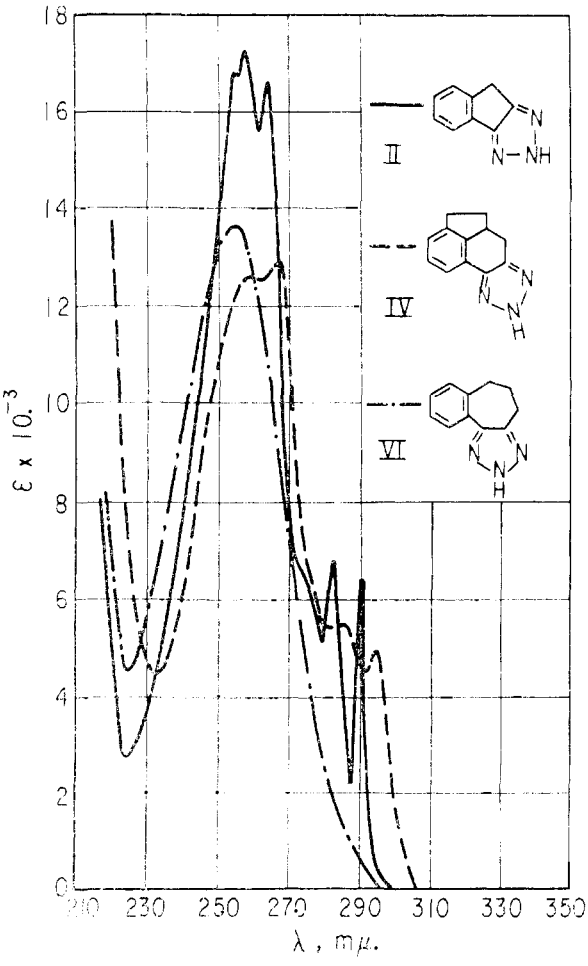


Fig. 1.—Ultraviolet absorption spectra in methanol of: indano[1,2-d]-*v*-triazole (II), ———; 2a,3,4,5-tetrahydroacenapho-[4,5-d]-*v*-triazole (IV), – – – –; and 1,2-benzocyclohepteno-[3,4-d]-*v*-triazole (VI), — – —.

The characteristic absorptions in the infrared for *v*-triazole ring vibrations have been assigned[5,6] to two bands in the regions 8.90–9.25 μ (1123–1080 cm.$^{-1}$) and 10.05–10.23 μ (995–977 cm.$^{-1}$), and these are present in all four of the new triazoles. Only those bands are given which are absent in the spectra of the corresponding hydrazone oximes.

(6) E. Lieber, C. N. R. Rao, T. S. Chao and H. Rubinstein, *Can. J. Chem.*, **36**, 1441 (1958).

Discussion

As has been demonstrated, when the hydrazones of α-oximinoketones are heated with potassium hydroxide in diethylene glycol at 170–190°, there are two possible reactions which can occur. If the hydrazone oxime is acyclic, that is, if the two functional groups can assume a skew configuration relative to each other, then the reaction which predominates to the exclusion of any other is normal Wolff-Kishner reduction of the hydrazone to methylene, yielding the corresponding oxime. Aliphatic ketoximes are reasonably stable under these conditions, while aldoximes and ketoximes with a benzylic α-carbon (such as XVII) are unstable to hot akali and react to produce various other products.

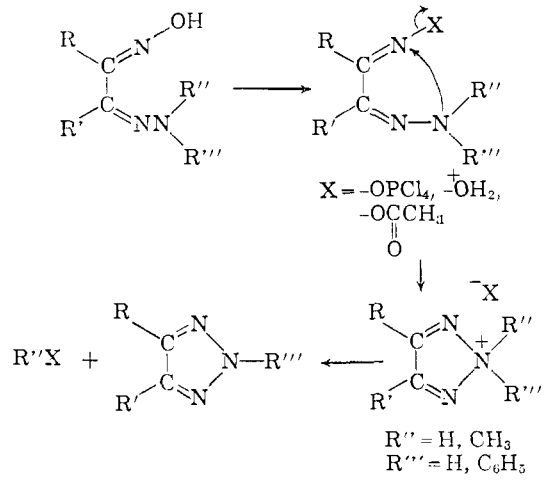
If the hydrazone and oxime functions form part of an alicyclic ring, normal Wolff–Kishner reduction can still take place as in the conversion of camphorquinone-2-hydrazone-3-oxime (IX) in part to epicamphor oxime (X), but a second, competing reaction can also occur—that of triazole formation, as illustrated by the partial conversion of IX to camphanotriazole (XI). Unlike normal Wolff–Kishner reduction, triazole formation appears to take place only if the hydrazone and oxime functions are more or less rigidly held in a co-planar configuration as they are in IX and more so in indandione 1-hydrazone 2-oxime (I); in the latter case triazole formation becomes the predominant reaction. As the size of the ring increases, the possibility of the functional groups assuming skew configurations is greater and, hence, the yield of triazole is only 15% in the case of the seven-membered ring compound V.

Although the triazoles were the only products characterized from the reactions of I, III and V, it is possible that these three compounds also undergo some normal Wolff–Kishner reduction concurrently, since the corresponding products would all be ketoximes with benzylic α-carbons and like phenylacetone oxime (XV) might be unstable under the reaction conditions. In support of this possibility is the fact that considerable non-volatile material is isolated from the reactions of I, III and V.

The question then arises as to what is the mechanism of triazole formation under these alkaline conditions. The previously reported conversions of hydrazone oximes to triazoles have all been carried out in acidic media. Clearly the mechanism is quite different in these cases from that of the alkali-catalyzed triazole synthesis. Several particulars about the acid-catalyzed reaction may be mentioned: (1) there is no such rigid steric requirement, (2) such reagents as acetic anhydride[7–9] phosphorus pentachloride[10] and aqueous hydroxylamine hydrochloride[11] effect the conversion of acyclic hydrazone oximes to triazoles quite readily, (3) the Wolff–Kishner reaction is not an alternative in these cases. A generalized mechanism for triazole formation under acidic

(7) A. Jonas and H. von Pechmann, *Ann.*, **262**, 277 (1891).
(8) O. Baltzer and H. von Pechmann, *ibid.*, **262**, 302 (1891).
(9) M. Ruccia, *Ann. chim. (Rome)*, **50**, 1363 (1960).
(10) H. von Pechmann, *Ber.*, **21**, 2751 (1888).
(11) K. Auwers and M. Siegfeld, *ibid.*, **26**, 788 (1893).

conditions may be formulated as



In the contrasting case of triazole formation reported in the present work, a number of major differences are apparent. Firstly, alkali is a necessity, no triazole being isolated when a solution of 1,2-indandione 1-hydrazone 2-oxime is heated at 170–190° in diethylene glycol without potassium hydroxide. Thermal decomposition to polymeric material takes place.

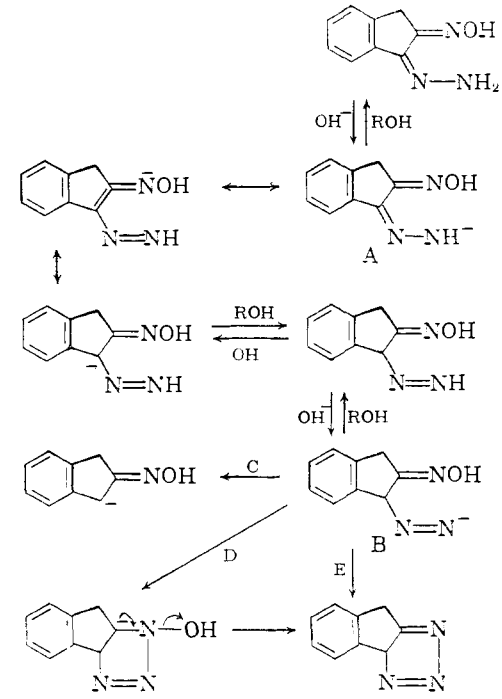
Secondly, the degree of substitution of the hydrazone nitrogen is of definitive importance. If both hydrogens are not present on this nitrogen, triazole formation does not take place.

As examples, both 1,2-indandione 1-phenylhydrazone 2-oxime and 1,2-indandione 1-methylhydrazone 2-oxime were subjected to Wolff–Kishner conditions. 1,2-Indandione 1-phenylhydrazone 2-oxime yielded no triazole, only polymeric material being obtained. 1,2-Indandione 1-methylhydrazone 2-oxime also yielded almost entirely non-volatile material; however, a very small amount (about 1%, compared with a 52% yield from the unmethylated hydrazone oxime) of 2-methylindano[1,2-d]-*v*-triazole was formed. To establish that these results were due to the lack of triazole formation and not the instability of the 2-substituted triazoles, both 2-methyl- and 2-phenylindano[1,2-d]-*v*-triazoles were prepared independently by acid-catalyzed cyclization. After being subjected to the reaction conditions, they were recovered quantitatively and unchanged. This establishes that the overwhelmingly predominant course of triazole formation in alkali requires an unsubstituted hydrazone nitrogen.

The third difference, of course, is the competing normal Wolff–Kishner reduction.

A mechanism that accounts for all these observations is given.

The resonance stabilized anion A, by addition and removal of a proton, is converted to the anion B, which is the common intermediate for both normal Wolff–Kishner reduction (path C) and triazole formation and rationalizes the need for an unsubstituted hydrazone nitrogen. Triazole formation may occur by addition followed by hydroxyl displacement (path D) or by direct displacement of the hydroxyl group (path E). On



the basis of this interpretation, the steric factors will be the most important in determining which course the reaction takes.

Experimental[12]

1,2-Indandione 1-Hydrazone 2-Oxime (I).—1,2-Indandione 2-oxime[13] (1.61 g., 10.0 mmoles), 30 ml. of purified[14] diethylene glycol and 2.1 ml. of 85% hydrazine hydrate was heated at 120° for 3 hours. Upon cooling, the solution yielded colorless needles which were filtered. The mother liquor was diluted with 40 ml. of water and extracted with four 50-ml. portions of methylene chloride. The residue left after evaporating the methylene chloride was combined with the previous crystals, and crystallization from ethanol yielded 1,2-indandione 1-hydrazone 2-oxime (I, 1.65 g., 9.35 mmoles, 93.5% yield), m.p. 240–242° dec.

Anal. Calcd. for $C_9H_9N_3O$: C, 61.7; H, 5.2; N, 24.0. Found: C, 61.9; H, 5.2; N, 24.1.

Indano[1,2-d]-*v*-triazole (II).—1,2-Indandione 1-hydrazone 2-oxime (I, 930 mg., 5.3 mmoles) and potassium hydroxide (1.23 g., 22 mmoles) in 50 ml. of purified diethylene glycol was subjected to the following general procedure, hereafter referred to as the standard Wolff–Kishner reaction: The solution was heated with a stream of nitrogen bubbling through it until the temperature reached 170°–190° (*ca.* 30 min.). Heating was maintained at 170–190° for 3 hours and nitrogen was bubbled through the solution for the entire time. The mixture was then cooled and subjected to a standard product isolation procedure as follows:

The mixture was diluted with 400 ml. of 1 *N* aqueous potassium hydroxide and extracted with four 200-ml. portions of methylene chloride. Each methylene chloride wash was back-washed with two 100-ml. portions of saturated aqueous sodium chloride. The methylene chloride extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated *in vacuo* to yield the neutral fraction. The alkaline solution was acidified with hydrochloric acid, and the *p*H was adjusted to 7 with sodium bi-

(12) All melting points were taken on the Kofler hot-stage. Microanalyses were performed by V. Tashinian, Microchemical Laboratory, University of California, Berkeley. Infrared spectra were taken in chloroform except for those of compounds I–VI, which were taken in potassium bromide. Ultraviolet spectra were taken in methanol.

(13) S. Gabriel and R. Stelzner, *Ber.*, **29**, 2603 (1896).

(14) Diethylene glycol was purified by stirring overnight on a steam-bath with solid sodium hydroxide (5 g./100 ml.) and distilling at reduced pressure, b.p. 126° (12 mm.).

carbonate. The solution was again extracted with four 200-ml. portions of methylene chloride, these organic extracts being treated the same as above and evaporated to yield the weakly acidic fraction. Hydrochloric acid then was used to acidify the solution of *p*H 2, and the aqueous layer was again extracted with four 200-ml. portions of methylene chloride, the extracts being treated as above to yield the strongly acidic fraction. In this manner, 200 mg. of material was found in the neutral fraction, 584 mg. in the weakly acidic fraction and nothing in the strongly acidic fraction.

The neutral fraction consisted entirely of non-volatile (at 140°, 0.15 mm.), polymeric material. The weakly acidic fraction was sublimed at 100°, 0.2 mm. to yield 432 mg. (2.75 mmoles, 52%) of indano[1,2-d]-*v*-triazole (II) which was dried at 60° (0.03 mm.) for 10 hr.; m.p. 143.5–144°, reported[8] m.p. 140–141.5°.

Anal. Calcd. for $C_9H_7N_3$: C, 68.8; H, 4.5; N, 26.8. Found: C, 68.9; H, 4.7; N, 26.8.

The Wolff–Kishner Reaction with 1,2-Indandione 1-Phenylhydrazone 2-Oxime.—1,2-Indandione-2-oxime[13] (5.1 g., 32 mmoles), and 4 ml. of phenylhydrazine in ethanol to which a few drops of glacial acetic acid had been added, were boiled 1 hour. Water was added to turbidity and the hot solution clarified with ethanol. On cooling, 7.2 g. of yellow needles (29 mmoles, 91%) was obtained, m.p. 178–179° after recrystallization from ethanol–water.

Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.7; H, 5.2; N, 16.7. Found: C, 71.9; H, 5.0; N, 16.8.

A solution of 2.67 g. of the phenylhydrazone oxime and 2.06 g. of potassium hydroxide in 80 ml. of purified diethylene glycol was subjected to the standard reaction and isolation procedure as outlined above. There was obtained a neutral fraction (2.06 g.), a weakly acidic fraction (0.07 g.) and a strongly acidic fraction (0.02 g.). The products were completely intractible; no triazole was obtained.

The Wolff–Kishner Reaction with 1,2-Indandione 1-Methylhydrazone 2-Oxime.—The procedure of Robert[15] was used to prepare ethanolic aqueous methylhydrazine acetate. Methylhydrazine sulfate (5 g.) in 20 ml. of boiling water was treated with potassium acetate (10 g.). The solution was boiled a few minutes, then cooled somewhat. Ethanol (20 ml.) was added, and the precipitated potassium sulfate removed by filtration. The filtrate was added to 1,2-indandione 2-oxime (2.84 g., 17.6 mmoles), and the solution was boiled for 1 hour. Water was added to precipitate the crude product (2.14 g., 11.3 mmoles, 64%) which was recrystallized twice from ethanol to yield 1,2-indandione 1-methylhydrazone 2-oxime, m.p. 188–189°.

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.5; H, 5.9; N, 22.2. Found: C, 63.2; H, 5.9; N, 22.3.

The methylhydrazone oxime (4.37 g.) and potassium hydroxide (3.1 g.) in 90 ml. of diethylene glycol was subjected to the standard Wolff–Kishner conditions outlined above, and the isolation procedure applied, yielding 3.62 g. of neutral fraction and 0.22 g. of weakly acidic fraction. The neutral fraction was sublimed at 140–150° (0.15 mm.). Only 159 mg. of a viscous oil was obtained, the remaining material being non-volatile, as was the weakly acidic fraction. On the basis of combustion analysis and ultraviolet absorption, this oil was found to contain no more than 58% triazole.

The following **hydrazone oximes** were prepared by treating the corresponding oxime with hydrazine hydrate in refluxing ethanol.

A. **2a,3,4,5-Tetrahydro-4,5-acenaphthenedione 4-oxime 5-hydrazone** (III) was prepared from 2a,3,4,5-tetrahydro-4-oximino-5-acenaphthenone[16] and was crystallized from chloroform; m.p. 154–155°.

Anal. Calcd. for $C_{12}H_{13}N_3O$: C, 66.9; H, 6.1; N, 19.5. Found: C, 66.5; H, 6.1; N, 19.3.

B. **1,2-Benzo-3,4-cycloheptenedione 3-hydrazone 4-oxime** (V) was prepared from α-oximinobenzosuberone (m.p. 139–140°, reported[17] m.p. 133–134°) and was crystallized from ethanol; m.p. 159–160°.

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.0; H, 6.5; N, 20.7. Found: C, 65.2; H, 6.7; N, 20.8.

C. The method of Francesconi and Pirazzoli[18] was used to prepare acenaphthenequinone monoxime. Monoxime thus prepared was contaminated with some dioxime which cannot be removed by recrystallization. The **acenaphthenequinone hydrazone oxime** (VII) which precipitated from boiling ethanol melted at 223–225° dec.

Anal. Calcd. for $C_{12}H_9N_3O$: C, 68.2; H, 4.3; N, 19.9. Found: C, 67.3; H, 4.3; N, 19.4.

D. **Camphorquinone 2-Hydrazone 3-Oxime** (IX). Camphor was oximinated according to the method of Claisen.[19] The alkaline solution of the sodium salt of α-oximinocamphor was washed in the cold and dark with ether and then was treated with acetic acid.[20] The *syn* isomer which precipitated was crystallized from benzene, m.p. 153–155°, indicating that the compound is pure *syn*-camphorquinone 3-oxime.[19] The infrared absorption of 1% and 12.5% solutions in chloroform provided further evidence for the internal hydrogen bonding characteristic of the *syn* isomer. The camphorquinone 2-hydrazone 3-oxime was crystallized from hexane–benzene; m.p. 125–126°.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8; N, 21.5. Found: C, 62.3; H, 8.8; N, 21.2.

E. **2,3-Octanedione 2-hydrazone 3-oxime** (XV) was prepared from 2,3-octanedione 3-oxime[21] and was crystallized from chloroform–hexane; m.p. 68–70°.

Anal. Calcd. for $C_8H_{17}N_3O$: C, 56.1; H, 10.0; N, 24.5. Found: C, 55.7; H, 10.2; N, 24.7.

F. **Biacetyl hydrazone oxime** (XVI), prepared from biacetyl monoxime,[22] was crystallized from chloroform; m.p. 131–132° (reported[23] m.p. 140°).

Anal. Calcd. for $C_4H_9N_3O$: C, 41.7; H, 7.9. Found: C, 41.6; H, 8.3.

G. **α-Oximinopropiophenone hydrazone** (XIV) was prepared from α-oximinopropiophenone and was crystallized from ethanol; m.p. 186–187°.

Anal. Calcd. for $C_9H_{11}N_3O$: C, 61.0; H, 6.3; N, 23.7. Found: C, 60.8; H, 6.3; N, 24.0.

The Wolff–Kishner Reaction with the following hydrazone oximes was carried out in each instance according to the standard reaction and isolation procedure given above.

A. From the reaction with 2a,3,4,5-tetrahydro-4,5-acenaphthenedione 4-oxime 5-hydrazone (III, 1.05 g., 4.9 mmoles), a neutral fraction (0.54 g.) was obtained from which no identifiable products could be isolated. From the weakly acidic fraction (0.42 g.), sublimation at 120° (0.15 mm.) yielded 330 mg. (1.7 mmoles, 34%) of **2a,3,4,5-tetrahydroacenaphtho[4,5-d]-*v*-triazole** (IV), m.p. 204–205.5°.

Anal. Calcd. for $C_{12}H_{11}N_3$: C, 73.1; H, 5.6; N, 21.3. Found: C, 72.7; H, 5.9; N, 21.3.

B. From the reaction with 1,2-benzo-3,4-cycloheptenedione 3-hydrazone 4-oxime (V, 2.08 g., 10.2 mmoles), a neutral fraction of 1.37 g. and a weakly acidic fraction of 0.36 g. were obtained. The weakly acidic fraction was sublimed at 140° (0.15 mm.) to yield 280 mg. (1.51 mmoles, 15% yield) of **1,2-benzocyclohepteno[3,4-d]-*v*-triazole** (VI), m.p. 215–216°.

Anal. Calcd. for $C_{11}H_{11}N_3$: C, 71.3; H, 6.0; N, 22.7. Found: C, 71.5; H, 6.2; N, 22.4.

The neutral fraction was subjected to chromatography on 50 g. of acid-washed alumina. Benzene eluted a yellowish substance of waxy appearance. Subsequent elution by methylene chloride and chloroform yielded only amorphous non-volatile gums. The substance eluted by benzene was sublimed at 100° (0.15 mm.) to yield 150 mg. of white crystals contaminated with some yellow gum. Recrystallization from ethanol afforded white crystals which were dried at 20° (0.2 mm.) for 24 hr.; m.p. 168–170°.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.0; H, 7.0; N, 8.9. Found: C, 83.8; H, 6.5; N, 9.0.

(15) J. L. Robert, *Rec. trav. chim.*, **56**, 413 (1937).

(16) H. Rapoport and J. Z. Pasky, *J. Am. Chem. Soc.*, **78**, 3788 (1956).

(17) W. Borsche and A. Roth, *Ber.*, **54**, 174 (1921).

(18) L. Francesconi and F. Pirazzoli, *Gazz. chim. ital.*, **33**, 36 (1903).

(19) L. Claisen and O. Manasse, *Ann.*, **274**, 71 (1893).

(20) M. O. Forster and K. A. N. Rao, *J. Chem. Soc.*, 2670 (1926).

(21) L. Behr-Bregowski, *Ber.*, **30**, 1515 (1897).

(22) W. L. Semon and V. R. Damerell, *J. Am. Chem. Soc.*, **47**, 2033 (1925).

(23) M. O. Forster and B. B. Dey, *J. Chem. Soc.*, **101**, 2234 (1912).

C. From the reaction with acenaphthenequinone hydrazone oxime (VII, 756 mg., 3.6 mmoles), 210 mg. of **acenaphthenone oxime** (VIII) was isolated from the weakly acidic fraction; m.p. 175–180° dec. (reported[24] m.p. 175°).

D. From the reaction with camphorquinone 2-hydrazone 3-oxime (IX, 1.29 g., 6.6 mmoles), a weakly acidic product (403 mg.) was obtained which was sublimed, giving 369 mg. of crystals (2.1 mmoles, 32%). Crystallization from benzene–hexane and resublimation yielded **camphano[2,3-d]-*v*-triazole (XI)**, m.p. 124–137°.

Anal. Calcd. for $C_{10}H_{15}N_3$: C, 67.8; H, 8.5; N, 23.7. Found: C, 67.6; H, 8.5; N, 23.6.

The neutral product (790 mg.) was chromatographed on 25 g. of acid-washed alumina. The bulk of the material was eluted by methylene chloride, and this material was sublimed to yield 640 mg. (3.8 mmoles, 58%) of **epicamphor oxime X**, m.p. 104–105° and $[\alpha]_D^{25}$ 98.5° (*c* 4.0, benzene) after recrystallization from aqueous methanol (reported[25] m.p. 103–104°, $[\alpha]_D$ 100.5°).

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.8; H, 10.3; N, 8.4. Found: C, 71.5; H, 10.5; N, 8.7.

D. From the reaction with 2,3-octanedione-2-hydrazone-3-oxime (XVI, 3.14 g., 18.3 mmoles), the neutral fraction (1.86 g.) obtained was chromatographed on acid-washed alumina (40 g.) and was separated into **3-octanone** (507 mg., 4.0 mmoles, 21%) and **3-octanone oxime** (1.33 g., 9.3 mmoles, 50%). Both products had identical infrared spectra and retention times on vapor phase chromatography with authentic samples and differed significantly from the corresponding 2-isomers. **The 3-octanone oxime** was prepared in the usual manner from 3-octanone and had b.p. 89° (6 mm.), n_D^{16} 1.4546 (reported[26] b.p. 92° (5 mm.), n_D^{20} 1.4517).

Anal. Calcd. for $C_8H_{17}NO$: C, 67.1; H, 12.0; N, 9.8. Found: C, 67.0; H, 12.0; N, 9.8.

E. From the reaction with biacetyl hydrazone oxime (XVII, 2.20 g., 19.1 mmoles), a weakly acidic fraction (700 mg.) and a neutral fraction (175 mg.) were obtained. Both were shown to be **methyl ethyl ketoxime** (52% yield) by direct comparison with an authentic sample.

F. From the reaction with α-oximinopropiophenone hydrazone (XIV, 4.7 g.), the only identifiable product was about a 5% yield of benzoic acid in the strongly acidic fraction. Exactly the same result was obtained with phenylacetone oxime. In both cases, the majority of the material remained as polymeric material in the neutral fraction.

G. From the reaction with α-oximinoacetophenone hydrazone[27] (XIII, 1.16 g., 7.1 mmoles), a strongly acidic fraction (758 mg., 5.6 mmoles, 78%) was obtained and was identified as **phenylacetic acid.**

Phenylacetaldoxime[28] (1.17 g., 8.6 mmoles) and potassium hydroxide (2.4 g., 43 mmoles) in 80 ml. of diethylene glycol gave as the only significant product a strongly acidic fraction (945 mg., 6.9 mmoles, 80%), also identified as **phenylacetic acid.**

2-Methylindano[1,2-d]-*v*-triazole.—1,2-Indandione 1-methylhydrazone 2-oxime in acetic anhydride was heated at reflux for 1 hour. Water was then added, the solution was made alkaline with 3 *N* sodium hydroxide, and 1% potassium permanganate solution was added until the purple color persisted. The mixture was extracted with an equal volume of methylene chloride (in two portions), and the residue after evaporating the methylene chloride was chromatographed on alumina. Benzene eluted the 2-methylindano[1,2-d]-*v*-triazole, m.p. 58–59°; ultraviolet absorption: λ_{max} 261 mμ (ε 19,000), 268 (18,500), 285 (10,500), 293 (11,700).

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.2; H, 5.3; N, 24.5. Found: C, 70.3; H, 5.3; N, 24.2.

2-Phenylindano[1,2-d]-*v*-triazole was prepared from 1,2-indandione 1-phenylhydrazone 2-oxime and acetic anhydride by the procedure described above for the 2-methyl analog. On recrystallization from benzene–hexane, it melted at 129–130° (reported[29] m.p. 125°); ultraviolet absorption: λ_{max} 223 mμ (ε 10,600), 287 (18,000), 311 (36,900).

Anal. Calcd. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.8; N, 18.0. Found: C, 77.3; H, 4.7; N, 18.1.

(24) C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).
(25) J. Bredt and W. H. Perkin, *J. Chem. Soc.*, **103**, 2182 (1913).
(26) F. Asinger, G. Geiseler and P. Laue, *Ber.*, **90**, 485 (1957).
(27) B. B. Dey, *J. Chem. Soc.*, **105**, 1039 (1914).
(28) R. A. Weerman, *Ann.*, **401**, 1 (1913).
(29) G. Charrier, *Gazz. chim. ital.*, **58**, 254 (1928).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN., AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA, GAINESVILLA, FLA.]

Molecular Rearrangements. XIX. The Thermal Decomposition of N-Acetyl-N-nitroso-1,2,2-triphenylethylamine[1]

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Several isotope position isomers of N-acetyl-N-nitroso-1,2,2-triphenylethylamine (III) have been prepared in optically active form. The thermal decompositions of these in *p*-cymene and in glacial acetic acid at several temperatures have been followed kinetically. The product, partially racemic 1,2,2-triphenylethyl acetate (IV), has been resolved, and the carbon-14 distributions in each enantiomer have been determined. The nitrosoamide IIIa, labeled in the 1-position with carbon-14, has been subjected to thermal decomposition also in propionic acid, and the yields of acetate IV and propionate VI have been determined. Both exhibit scrambling of their chain labels. The identification of labeled acetoxyl with D-(+)-1,2,2-triphenylethyl acetate (IVc) in the thermal decomposition of (−)-IIIc in glacial acetic acid establishes the D-configurations of (+)-I, (+)-II and (−)-III. Optically active 1,2,2-triphenylethyl-1-C^{14}-amine (Ia) has been deaminated in glacial acetic acid containing sodium acetate, the partially racemic product IVab has been resolved and the carbon-14 distribution in each enantiomer has been determined. The extent of inversion during each reaction was measured. All results are explained in terms of a mechanism involving ion pairs of the acetoxyl anion with equilibrating, classical triphenylethyl carbonium ions.

Introduction

The stereochemistry of the deamination of 1,2,2-triphenylethylamine in aqueous solution containing a small concentration of acetic acid has been reported.[4] Thus D-(+)-1,2,2-triphenylethyl-

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(4) C. J. Collins, W. A. Bonner and C. T. Lester, *ibid.*, **81**, 466 (1959).