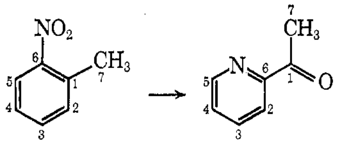
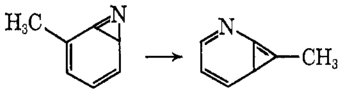
Taken in connection with earlier data on nitroxylenes,[5] these results define the structural relationship between o-nitrotoluene and 2-acetylpyridine, as shown



above. These data rule out our most recent mechanistic proposal.[5] Other proposals[9,10] are in accord with these results, although the nature of the rearranged intermediate and its relationship to the azirine **12** remain incompletely defined. The azirine **12** may be formed and undergo further skeletal rearrangement to **13**.[10] However, an intermediate containing the rearranged skeleton and a molecule of triethyl phosphite cannot be ruled out at this point.



12 **13**

Experimental Section

o-Nitroluene-1-^{14}C.—Toluene-1-^{14}C (9.2 g, 0.1 mol, 50 μCi, New England Nuclear) was nitrated using the procedure of Hurd and Jenkins.[11] Vacuum distillation of the product using a 290-mm spinning-band still gave o-nitrotoluene (4.48 g) containing 11% *para* isomer. A second fraction (1.38 g, 79% pure) was also colected.

Photolysis of o-Nitrotoluene-1-^{14}C in Triethyl Phosphite.—o-Nitrotoluene (6.85 g, 0.0500 mol, 0.51 × 10^6 dpm/mmol, 5.5% *p*-nitrotoluene impurity) was dissolved in freshly distilled triethyl phosphite (*ca.* 190 ml) and the solution was flushed with nitrogen for 30 min and then photolyzed for 24 hr using a type S 200-W Hanovia mercury lamp and Pyrex filter. A nitrogen flow was maintained through the solution during the photolysis. The unreacted triethyl phosphite was distilled from the reaction mixture, bp 25–30° (0.3 mm), followed by a fraction, bp 30–62° (0.25 mm), containing triethyl phosphate and o-nitrotoluene. The residue was mixed with 10% hydrochloric acid (100 ml) and continuously extracted with ether for 24 hr. The aqueous layer was separated and made alkaline with 30% sodium hydroxide. The solution was extracted with ether. The extract was dried, concentrated, and distilled, giving a mixture containing 2-acetylpyridine (0.44 g, 0.0036 mol, 14%) and o-toluidine (1.26 g, 0.0118 mol, 24%) as indicated by nmr analysis.

2-(Acetyl-1-^{14}C)pyridine Oxime (7).—The mixture of **5** and **6** described above was added to a solution of hydroxylamine hydrochloride (1.4 g) and sodium hydroxide (0.8 g) in water (10 ml). The resulting mixture was stirred at room temperature for 20 hr. The pH was adjusted to 7 with acetic acid and the solution was extracted with ether. The ether was dried (potassium carbonate) and evaporated, leaving an oil from which the oxime crystallized. The solid was washed with petroleum ether, giving **7** (0.247 g), mp 117–118° (lit.[12] mp 121°), having an ir spectrum identical with that of an authentic sample.

N-(2-Pyridyl)acetamide-1-^{14}C (8).—2-Acetylpyridine oxime (0.236 g, 0.00173 mol) was dissolved in anhydrous ether (5 ml) and the solution was cooled in ice. Phosphorus pentachloride (0.530 g, 0.00255 mol) was added with stirring to the cooled solution. The solution was stirred for 30 min at 0° and then refluxed gently for 1.25 hr. The reaction mixture was poured onto ice. The resulting aqueous solution was made alkaline with 30% sodium hydroxide and extracted with ether. The crude product obtained by evaporation of the ether was triturated with hexane and filtered, giving **8** (0.145 g, 61%), mp 61–65° (lit.[13] mp 71°), having an ir spectrum identical with that of an authentic sample.

Hydrolysis of N-(2-Pyridyl)acetamide-1-^{14}C.—A solution of **8** (0.218 g, 0.00160 mol) in 6 *N* hydrochloric acid (5 ml) was refluxed for 3 hr. The solution was cooled, made alkaline with 30% sodium hydroxide, extracted with ether, dried over potassium carbonate, and evaporated to give 2-aminopyridine (0.128 g, 0.00136 mol, 85%), mp 53–55°, 55–57° after recrystallization from hexane (lit.[14] mp 56°).

Evaporation of the aqueous alkaline solution gave residual salts (1.88 g) which were used in the Schmidt degradation described below.

Schmidt Reaction on Sodium Acetate.[15]—The residual salts were mixed with concentrated sulfuric acid (6 ml) and cooled to 0°, and sodium azide (0.31 g) was added. The reaction was swept with carbon dioxide free nitrogen which was then passed through 5% potassium permanganate in 5% sulfuric acid into barium hydroxide solution. The reaction flask was heated at 80–85° for 2.5 hr and 64 mg of barium carbonate was collected.

Counting Procedures.—Samples of compounds **2**, **3**, **7**, **8**, and **9** were counted in toluene solution (10 ml) containing 4.0 g/l. of POP and 50.0 mg/l. of POPOP on a Nuclear-Chicago Model 723 counter. Counting efficiencies, as determined from a standard channels-ratio quenching curve, ranged from 69 to 81%. The barium carbonate was counted on a planchet using a Nuclear-Chicago 2-π gas-flow low-background counter. Dilutions with inactive materials were made during the degradative scheme, as noted in Table I.

Registry No.—**2**, 22794-71-4; **3**, 22794-72-5; **7**, 22866-46-2; **8**, 22794-73-6; **9**, 504-29-0.

Acknowledgment.—We thank Professor Oscar R. Rodig for advice on technique and counting procedures.

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Studies of Nitriles. II.[1a] Synthesis of β,β-Dichloroacrylonitrile and Its Reactions with Some Nucleophilic Reagents[1b]

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β,β-Dichloroacrylonitrile (I) was first prepared by Miller and Kalnins[2] in 1967 by reducing α-acetoxy-β,-β,β-trichloropropionitrile with zinc dust in boiling THF. The previous paper[1a] dealt with a novel pyrolytic coupling reaction of chloroacetonitrile. Now the proposed mechanism of the reaction led us to an idea that, when carbon tetrachloride or chloroform is pyrolyzed with acetonitrile, β,β-dichloroacrylonitrile would probably be obtained as depicted by the following reactions.

$$CCl_4 \longrightarrow \cdot CCl_3 + \cdot Cl \qquad (1)$$

$$Cl\cdot + CH_3CN \longrightarrow \cdot CH_2CN + HCl \qquad (2)$$

$$\cdot CCl_3 + \cdot CH_2CN \longrightarrow Cl_3CCH_2CN \qquad (3)$$

$$Cl_3CCH_2CN \longrightarrow Cl_2C{=}CHCN + HCl \qquad (4)$$

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[1] (a) Paper I: N. Hashimoto, K. Matsumura, and K. Morita, *J. Org. Chem.*, **34**, 3410 (1969); (b) presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1968.

[2] B. Miller and M. V. Kalnins, *Tetrahedron*, **23**, 1145 (1967).

TABLE I

CONDITIONS AND RESULTS OF THE COPYROLYSIS OF ACETONITRILE AND CARBON TETRACHLORIDE

Starting mixtures		CCl_4/CH_3CN mole ratio	Reaction temp, °C	Pressure, mm	Reaction time, min	Amount of recovd compd		Yield of $Cl_2C{=}CHCN$, g,[a] %[b]	Yield of $ClC{\equiv}CCN$, g[c]	Total yield, %[d]
CCl_4, g	CH_3CN, g					CCl_4, g	CH_3CN, g			
15.4	4.1	1:1	900	27	40	0.5		1.8, 15	1.15	28
15.4	8.2	1:2	900	25	80	1.4	2.3	6.1, 55	0.54	62
15.4	16.4	1:4	900	20	60	2.9	10.0	4.8, 49	0.13	51
15.4	16.4	1:4	980	20	90	1.7	7.4	6.1, 56	0.69	65

[a] Yields of β,β-dichloroacrylonitrile were obtained by distillation. [b] Calculated on the basis of the converted CCl_4. [c] Determined by gas chromatography. [d] Based on the converted CCl_4.

This assumption was borne out by the experiment, in which mixtures of acetonitrile–carbon tetrachloride and acetonitrile–chloroform were pyrolyzed under reduced pressure at 800–1000° to give 50–60 and 14% yields of β,β-dichloroacrylonitrile, respectively. The mass spectrum of β,β-dichloroacrylonitrile reveals peaks at *m/e* 125, 123, and 121 (each corresponds to M^+) in the abundance ratio 1:6:9, which is in good accord with the theoretical ratio calculated for the molecular ion containing two chlorine atoms.

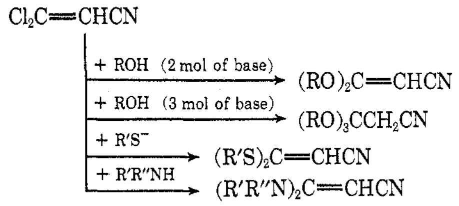
One remarkable thing which we have noted in our synthesis of dichloroacrylonitrile is that chlorocyanoacetylene is also formed as a by-product of the pyrolysis. After having been separated by the gas chromatographic technique, the structure of this compound was confirmed by the mass spectrum, which shows a very strong doublet at *m/e* 87 and 85 in the abundance ratio 1:3. The melting point of the isolated crystals was 42–43.5° (in a sealed tube) which was in good agreement with the value reported by Kloster-Jensen[3] (42–42.5°).

The detailed reaction conditions and results of some typical experiments are shown in Table I.

The conversion of carbon tetrachloride[4] was *ca.* 30% at 700°, *ca.* 80% at 800°, and *ca.* 90% at 900°, when an equimolar mixture of carbon tetrachloride and acetonitrile was allowed to react under the experimental conditions. Both high reaction temperatures and large excess of carbon tetrachloride over acetonitrile favored the formation of chlorocyanoacetylene, the formation of which may therefore be ascribed to the dehydrochlorination of β,β-dichloroacrylonitrile.

In order to obtain information on the mechanism of the present reaction, we irradiated a gaseous mixture of acetonitrile and carbon tetrachloride in a quartz tube with a low-pressure mercury lamp at room temperature. The gas chromatogram of the reaction mixture showed 5 peaks besides those of the starting materials, and the total yield of the products increased during 7 hr and thereafter gradually decreased. The conversion rate was rather low even at the highest conversion point. Four of the five products thus obtained were identified as Cl_3CCH_2CN, Cl_3CCCl_3, $(CH_2CN)_2$, and β,β-dichloroacrylonitrile by comparison of their retention time on gas chromatography with those of authentic samples. When a mixed solution of CH_3CN (1.64 g) and carbon tetrachloride (1.54 g) was irradiated for 7 hr, only two products (Cl_3CCCl_3 and $ClCH_2CN$) were seen on the gas chromatogram. The observed difference between the products of these photo- and thermo-induced reactions is interesting. It is not certain, at present, whether it is due to a temperature effect or the difference of the excitation states of the reactants.

Reactions of β,β-Dichloroacrylonitrile with Some Nucleophilic Reagents.—β,β-Dichloroacrylonitrile reacts with aliphatic alcohols and phenol in the presence of 2 mol equiv of base under mild conditions, giving good yields of cyanoketene acetals. With 3 mol equiv of sodium ethoxide in ethanol, cyanoacetic ortho ethyl ester was obtained in 72% yield together with 11% of cyanoketene diethyl acetal.



McElvain and Schroeder[5] have reported the synthesis of cyanoketene methyl and ethyl acetals *via* the corresponding cyanoacetic ortho esters, which they prepared from malononitrile. They also converted them into the corresponding cyanoacetic esters by treatment with acids. The reaction of β,β-dichloroacrylonitrile and tertiary alcohols did not proceed smoothly under similar conditions, therefore no further investigations were made. β,β-Dichloroacrylonitrile reacted smoothly with thiols in the presence of bases and gave the corresponding cyanoketene dithioacetals. With some amines, β,β-dichloroacrylonitrile reacted easily to give the derivatives of β,β-diaminoacrylonitrile. Curiously enough, however, β,β-dichloroacrylonitrile did not react in a straightforward manner with lower primary aliphatic amines and the reaction products could not be characterized. The reaction of β,β-dichloroacrylonitrile with ammonia was also sluggish and only a trace amount of malononitrile was yielded, as detected on thin layer and gas chromatograms.

Yields and physical constants of the cyanoketene derivatives thus obtained are summarized in Table II. In the fourth column of Table II, the characteristic values of the nmr chemical shifts of their α-olefinic protons (in $CDCl_3$) are listed. These values suggest that in these compounds, especially in cyanoketene acetals and aminals, the electron density on the α-carbon atom is increased owing to the presence of two electron-releasing groups on the β carbon. Further studies of the reactivity and synthetic utility of these derivatives will be reported elsewhere.

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[3] E. Kloster-Jensen, *Acta Chem. Scand.*, **18**, 1629 (1964).

[4] The yield of the reaction $2CCl_4 \rightarrow Cl_2C{=}CCl_2 + Cl_2$ is said to be 43% at 900–1000° and 80% at 1300–1400°, though care must be taken to avoid the recombination of the products: C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1929, p 132.

[5] S. M. McElvain and J. P. Schroeder, *J. Amer. Chem. Soc.*, **71**, 40, 47 (1949).

TABLE II

β,β-DISUBSTITUTED ACRYLONITRILES $(RX)_2C{=}CHCN$

$(RX)_2$	Registry no.	Yield, %	Bp (mm) [mp], °C	Hα, δ (ppm)[c]	Formula	Calcd, %			Found, %		
						C	H	N	C	H	N
$(CH_3O)_2$		83	60–61 (2.5) [42–43][a]	3.35							
$(C_2H_5O)_2$		78	98–98.5 (2) [37–38][b]	3.47							
$(n\text{-}C_3H_7O)_2$	22577-03-3	85	104–107 (2.5)	3.50	$C_9H_{15}NO_2$	63.88	8.94	8.28	63.59	9.11	8.30
$(i\text{-}C_3H_7O)_2$	22566-62-7	70	87–90 (2.5)	3.53	$C_9H_{15}NO_2$	63.88	8.94	8.28	63.59	8.90	8.31
$(n\text{-}C_4H_9O)_2$	22566-63-8	82	105–108 (2.5)	3.50	$C_{11}H_{19}NO_2$	66.97	9.71	7.10	66.76	9.80	6.94
$(i\text{-}C_4H_9O)_2$	22566-64-9	77	106–112 (2.5)	3.48	$C_{11}H_{19}NO_2$	66.97	9.71	7.10	66.77	9.84	7.27
$(s\text{-}C_4H_9O)_2$	22566-65-0	54	110–111 (2.5)	3.49	$C_{11}H_{19}NO_2$	66.97	9.71	7.10	66.83	9.61	7.14
OCH_2CH_2O	22577-04-4	35	124–126 (0.25) [84–85]	3.78	$C_5H_5NO_2$	54.05	4.54	12.61	53.84	4.44	12.41
$(PhO)_2$	22566-66-1	51	[73–74]	3.87	$C_{15}H_{11}NO_2$	75.93	4.67	5.90	75.81	4.46	5.90
$(n\text{-}C_4H_9S)_2$	22566-67-2	67	140–142 (2.5)	5.21	$C_{11}H_{19}NS_2$	57.59	8.35	6.11	57.78	8.27	6.48
$(PhCH_2S)_2$		86	Oil	4.85							
$(PhS)_2$				5.20							
$(CH_2CH_2OCH_2CH_2N)_2$	22566-69-4		[131–132]	3.37	$C_{11}H_{17}N_3O_2$	59.17	7.68	18.82	59.02	7.64	18.47
$(PhCH_2NH)_2$	22566-68-3	42	[95–96]	2.96	$C_{17}H_{17}N_3$	77.53	6.51	15.96	77.31	6.47	15.84

[a] Lit.[5] mp 41.5–42°, bp 127–128° (11 mm). [b] Lit.[5] mp 37–38°, bp 145–146° (20 mm). [c] Nmr chemical shift in $CDCl_3$.

Experimental Section

Copyrolysis of Acetonitrile with Carbon Tetrachloride.—The reaction was carried out in a horizontally mounted unpacked quartz tube, 1.2 cm in diameter and 60 cm in length, heated with two electric furnaces (15 and 20 cm in length, respectively). At one end of the tube was connected a sample inlet apparatus consisting of a buret and a vaporizing flask. The outlet of the tube was connected to a trapping system consisting of two trapping bottles cooled with Dry Ice–ethanol and a washing bottle containing acetone, cooled with Dry Ice–ethanol. Keeping the temperature of the furnaces at 700° (15 cm) and 900° (20 cm), the whole system was evacuated to *ca.* 20 mm with an aspirator, and mixtures of carbon tetrachloride and acetonitrile were introduced through a buret. From the reaction product were recovered the unchanged starting materials, together with a small amount of chlorocyanoacetylene. The remaining high-boiling product was analyzed by gas chromatography [column: TCP (10%) on Chromosorb W, 60–80 mesh, 1 m; column temperature, 120°] and subsequently subjected to fractional distillation. The results are summarized in Table I.

Identification of the Products.—β,β-Dichloroacrylonitrile was purified by distillation: bp 138–147° (lit.[2] 142–145°); ir (liquid film) 3050, 2220, 1589, 1490, 1272, 1140, 993, 960, 798, 667 cm^{-1}; nmr ($CDCl_3$) δ 5.89 (s); mass spectrum (70 eV) *m/e* 125, 123, 121, 88, 86, 62, 60, 51. (β,β-Dichloroacrylonitrile can be distinguished from the isomer, α,β-dichloroacrylonitrile, by direct comparison of the ir and nmr, as well as the boiling point.)

Reaction of β,β-Dichloroacrylonitrile with Alcohols. General Procedure.—To a stirred solution of sodium alkoxide, which was prepared by dissolving *ca.* 1.98 g of sodium metal in 50 ml of the corresponding alcohol, was added 5 g of β,β-dichloroacrylonitrile dropwise, under cooling with ice water. After being stirred for a few hours the solution was left to stand overnight at room temperature; then the alcohol was evaporated and water added to the residue. The mixture was neutralized with dilute HCl and extracted with ether or ethyl acetate. The extract was washed with water, dried, concentrated, and distilled, giving the corresponding β,β-dialkoxyacrylonitrile.

Reaction with Ethylene Glycol.—To a solution prepared by dissolving 3.28 of NaOH and 5.09 g of ethylene glycol in 60 ml of H_2O was added 5 g of β,β-dichloroacrylonitrile under cooling with ice water. After being left standing overnight at room temperature, the reaction mixture was neutralized with dilute HCl and extracted with ether. The extract was washed (H_2O), dried (Na_2SO_4), and concentrated to give a colorless solid (1.62 g), which was purified either by recrystallization from benzene or by distillation under reduced pressure to give 2-cyanomethylene-1,3-dioxolane.

Reaction with Phenol.—Sodium hydroxide (3.28 g) and phenol (7.72 g) were dissolved in 60 ml of water. To this solution with stirring under cooling, β,β-dichloroacrylonitrile (5 g) was added. The reaction mixture was stirred overnight at room temperature, then 5 hr at 100°, and extracted with ether. The extract was washed, dried, and concentrated to give a crystalline mass, which was recrystallized from ether–*n*-hexane to give β,β-diphenoxyacrylonitrile.

Reaction with Thiols or Thiophenols. General Procedure.—To a solution of sodium mercaptide, which was prepared by dissolving 2 mol of sodium hydroxide and the corresponding amount of mercaptan in 60 ml of 50% ethanol, β,β-dichloroacrylonitrile (5 g) was added dropwise under cooling. The reaction mixture was stirred at room temperature for *ca.* 15 hr, concentrated, and extracted with ether. The ether extract was washed, dried, and evaporated to give an oily material which was treated as follows.

Reaction with *n*-Butylmercaptan.—The product was distilled under reduced pressure to give pure β,β-dibutylthioacrylonitrile.

Reaction with Thiophenol.—The product was dissolved in acetone and treated with active carbon to give an almost pure oil: nmr ($CDCl_3$) δ 4.85 (s, 1), *ca.* 7.35 (almost s, 10).

Reaction with Benzylmercaptan.—The product was dissolved in ether and treated with active carbon to give an oily mixture of the products (total weight, 15.3 g) which contained *ca.* 70% β,β-dibenzylthioacrylonitrile and 30% dibenzyl sulfide. The former shows the following nmr peaks: ($CDCl_3$) δ 3.95 (s, 2), 4.20 (s, 2), 5.20 (s, 1), *ca.* 7.30 (10).

Reaction with Benzylamine.—Five grams of β,β-dichloroacrylonitrile was added dropwise to a stirred solution of benzylamine (17.6 g) in 100 ml of ether at an ice-chilled temperature. After being stirred at room temperature for 3 hr, the precipitate was filtered and washed with acetone. The combined solution of the washing and the filtrate was concentrated and the residue was recrystallized from benzene to give 4.5 g of β,β-dibenzylaminoacrylonitrile.

Reaction with Morpholine.—Morpholine (14.3 g) was dissolved in ether (100 ml) and to this solution, with stirring under cooling, β,β-dichloroacrylonitrile (5 g) was added dropwise. After stirring for 5 hr at room temperature, the reaction solution was left standing overnight at room temperature. Water was added to the solution and the ether layer was separated, washed, dried, and evaporated to give a small amount of crystalline mass, together with some oily substance. The former was separated by filtration and recrystallized from benzene–cyclohexane (1:1) to give β,β-dimorpholinoacrylonitrile.

Photoinduced Reaction of a Mixture of Carbon Tetrachloride and Acetonitrile.—In five quartz tubes of the same size (i.d. 7 mm, inner volume *ca.* 16 ml), the upper end of which was stopcocked, were placed *ca.* 32 mg (22 μl) of CCl_4 and 17 mg (22 μl) of CH_3CN, and the tubes were cooled with liquid nitrogen. After being evacuated with a vacuum pump at this temperature, the tubes were closed and warmed to room temperature, when *ca.* half of the content vaporized into a gaseous mixture. These tubes were affixed around a 40-W low-pressure mercury lamp and irradiated. After the irradiation of each for 3, 5, 7, 10, and 15 hr, the reaction tubes were detached one by one and opened. The contents of the tube were dissolved in 60 μl of acetone and analyzed by gas chromatography, which showed at least five prominent peaks. Four of them were identified as $ClCH_2CN$, $Cl_2C{=}CHCN$, Cl_3CCCl_3, and $(CH_2CN)_2$. The remaining one was unidentified.

Registry No.—I, 7436-85-3.

Acknowledgments.—The authors are grateful to Dr. S. Tatsuoka, General Manager of the Division, for encouragement throughout this work. Thanks are also due to Mr. M. Kan for the elemental analyses, to Mr. T. Shima for the measurement of mass spectra, and to Mr. K. Shinozaki for the measurement of nmr spectra.

Conversion of Certain Cyclic Phenylhydrazino Derivatives into Phenylazo Compounds with Periodic Acid[1]

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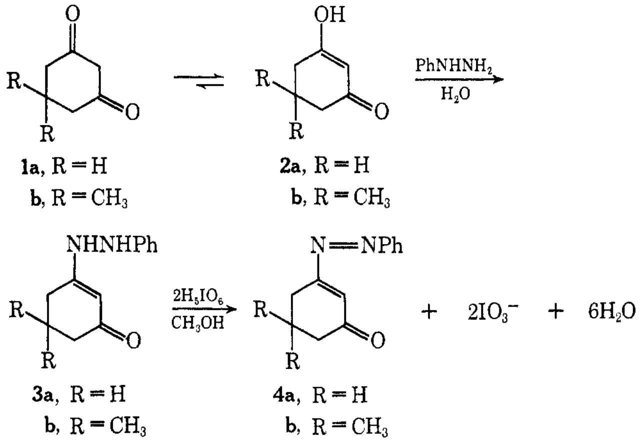
In connection with studies[3] of certain cyclic vinyl phenylazo compounds as possible intermediates in the formation of bis-[4] or trisphenylhydrazones,[5] there was a need to obtain pure samples of 3-oxo-1-phenylazo-1-cyclohexene (**4a**) and 5,5-dimethyl-3-oxo-1-phenylazo-1-cyclohexene (**4b**). One possible way to obtain these compounds is to convert the corresponding enols of 1,3-cyclohexanediones,[6] *e.g.*, the enol of 5,5-dimethyl-1,3-cyclohexanedione (**2b**), into the phenylhydrazino derivative **3b**; the oxidation of the latter would give the needed azo compound **4b**. This type of transformation was studied by Teuber,[7] Eistert,[8] and their students. Although the preparation of **4a** was described,[7] compound **4b** was not reported. In the preparation of **4a**, the starting intermediate, Merling's[9] "phenylhydrazone" **3a** was assigned the correct structure;[7,8] the vinyl structure of **3a** was also confirmed in this laboratory by nmr spectroscopy (see Experimental Section). Transformation of **3a** into **4a** was supposedly performed[7] in high yield by either autooxidation (bubbling of oxygen into an alkaline solution of **3a**) or by treatment with sodium chromate–acetic acid; however, details for isolation of **4a** were not given.[7] In another report,[8] conversion of **3a** into **4a** was performed with N-bromosuccinimide in boiling carbon tetrachloride (46% yield). Tlc [silica gel G, 1:9 ethanol–acetone (v/v), 3% periodic acid in methanol as the spray] revealed a trace of impurity in **4a** (mp 85–86°) prepared with N-bromosuccinimide as the oxidant;[8] this impurity can be formed by the bromination of a benzene ring or a labile vinyl bond of **4a**. However, this difficulty was overcome when periodic acid was used as the oxidant (or proton-abstracting agent); this reagent has proved to be a unique oxidant for other systems.[2]



1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

3a, R = H
b, R = CH_3

4a, R = H
b, R = CH_3

It has been found that treatment of a solution of **3a** or **3b** (1 mol) in methanol or glacial acetic acid with an aqueous solution of periodic acid (2 mol) at room temperature produces the corresponding azo compounds **4a** and **4b** in 90% yield. After recrystallization from aqueous acetic acid, 3-oxo-1-phenylazo-1-cyclohexene (**4a**) melted at 92–94°; it was homogeneous by tlc and the mass spectrum did not show impurity. For comparison, compound **3a** (1 mol) in glacial acetic acid was oxidized with lead tetraacetate (2.2 mol) to give the azo product **4a** in 55% yield; oxidation with sodium periodate gave the azo product in 70% yield. The moderate solubility of sodium periodate in water lessens its value as a preparatory reagent. (The product from the above two oxidations was isolated by extraction into chloroform.)

It is believed that clear-cut conversion of vinyl phenylhydrazino compounds **3a** and **3b** into the corresponding azo compounds **4a** and **4b** with periodic acid may indicate the general character of this reagent for deprotonation of this type of compound.

The action of periodic acid, a two-electron oxidant, on a phenylhydrazino group (conversion of **3a** and **3b** into **4a** and **4b**) can be envisaged as a simultaneous attack of an electrophilic and nucleophilic species (present in aqueous acetic acid–periodic acid) on vinyl and phenyl NH groups, respectively. This mechanistic approach is also in agreement with the earlier suggestion[2b,d] that the shift in equilibrium between electrophilic (nonionized) and ionized species of periodic acid solution is also dependent on the nature of the species to be oxidized.

The equation for calculation of the enol content of an acyclic β diketone[6d,e] was found to be useful in determination of the enehydrazine content in compounds **3a** and **3b**. The per cent of enehydrazine in a compound

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[1] Part V. For parts I–IV, see ref 2a–d, respectively.

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[3] A. J. Fatiadi, *Carbohyd. Res.*, **7**, 89 (1968).

[4] (a) L. Cagliotti, G. Rossi, and F. Rossi, *J. Amer. Chem. Soc.*, **88**, 3865 (1966); (b) H. Hassner and Catsoulacos, *Tetrahedron Lett.*, 489 (1967); (c) H. Simon, G. Heubuch, and H. Wacker, *Chem. Ber.*, **100**, 3106 (1967); (d) J. Buckingham. *Quart. Rev.* (London), **23**, 37 (1969).

[5] A. J. Fatiadi, to be published.

[6] The ring geometry of 1,3-cyclohexanedione (**1a**) and its 5,5-dimethyl derivative (**1b**) prohibits intramolecular rotation and intramolecular hydrogen bonding and so the enol of the dione becomes stabilized (*trans*-fixed enolization). Consequently, these 1,3-diones are almost completely enolized (95 and 100%, respectively); see (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 376–379; (b) B. Eistert and E. Merkel, *Chem. Ber.*, **86**, 896 (1953); (c) B. Eistert, E. Merkel, and W. Reiss, *ibid.*, **87**, 1513 (1954); compare with an enol form of an acyclic β diketone; (d) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964); (e) G. K. Schweitzer and E. W. Benson, *J. Chem. Eng. Data*, **13**, 452 (1968).

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