Treatment of **1** with molybdenum hexacarbonyl in refluxing *n*-hexane gave an off-white diamagnetic substance whose elemental analysis and vapor pressure osmometric molecular weight determination indicated the composition $(C_9H_{18}NO)_2Mo_3$. The infrared (ir) spectrum of the product (KBr) showed *no* terminal metal carbonyl stretching bands (2100–1800 cm^{-1}) but did exhibit intense absorption at 960, 926, and 808 cm^{-1} due, at least in part, to N–O stretching with oxygen coordination to the metal. The mass spectrum was similar to that reported by Morrison and Davies[13] for **1**. Although the structure of the product is not known, it is clear that deoxygenation does not occur here, in contrast to the results with $Fe_3(CO)_{12}$. Tungsten hexacarbonyl reacted with **1** to give a solid analogous to that obtained using $Mo(CO)_6$. Chromium hexacarbonyl failed to react with **1** under the described conditions.

Experimental Section

Melting points were determined on a Fisher-Johns or Gallenkamp apparatus and are uncorrected. Boiling points are also uncorrected. Elemental analyses were carried out by A. Bernhardt, West Germany, and Meade Microanalytical Laboratory, Amherst, Mass. Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer; the wavelength readings were calibrated with polystyrene film. Nmr spectra were obtained on a Varian A-60 spectrometer, employing tetramethylsilane as the internal standard.

The three iron carbonyls and chromium hexacarbonyl were purchased from Pressure Chemical Co. and were used as received. Climax Molybdenum Co. provided $Mo(CO)_6$ and $W(CO)_6$. Mr. William Moore prepared **1** following Rozantsev's procedure.[14] Radicals **3** and **5** were commercial products. All reactions were run under a nitrogen atmosphere.

Deoxygenation of Nitroxyl Radicals by $Fe_3(CO)_{12}$.—A mixture of $Fe_3(CO)_{12}$ (4.50 g, ~9 mmol), absolute methanol (2.0 ml), and dry benzene (50 ml) was refluxed with stirring for 6 hr. The nitroxyl radical (10 mmol), solid or in benzene (10–17 ml), was added to the iron hydride solution and the mixture was then refluxed for 9–18 hr. The solution was cooled and filtered, and work-up was effected in the following manner for the various reactions.

A. 2,2,6,6-Tetramethylpiperidine-1-oxyl.—The ir spectrum (neat) of the red oil, obtained on flash evaporation of the filtrate, showed it to consist largely of **2**, but a weak carbonyl stretching absorption at 1665 cm^{-1} indicated the possible presence of a small amount of *N*-formyl-2,2,6,6-tetramethylpiperidine. This by-product was also formed in reactions of **3** and **5**, but in all instances analytically pure samples could not be obtained owing to contamination by a metal carbonyl complex. The oil was repeatedly triturated with pentane. Flash evaporation of the dried pentane extract and subsequent distillation of the residue gave 0.59 g (42%) of 2,2,6,6-tetramethylpiperidine, bp 153–155° (lit.[15] bp 151–152°), identified by comparison with an authentic sample.

B. 4-Acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl.—The filtered material was washed well with dry ether, and the washings were added to the filtrate. Flash evaporation of the filtrate gave an oil, which was dissolved in ether. Pentane was then added until precipitation of **4** was complete. Filtration gave 1.10 g (55%) of 4-acetamido-2,2,6,6-tetramethylpiperidine, mp 118–120° (lit.[16] mp 120°).

C. 3-Carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl.—The filtered material was washed well with chloroform. Work-up as described in B gave **6** in 41% yield, mp 126.5–128.0° (lit.[17] mp 129–130°).

Reaction of 2,2,6,6-Tetramethylpiperidine-1-oxyl (1) with Group VI Metal Carbonyls.—A mixture of **1** (0.60 g, 3.85 mmol), $Mo(CO)_6$ (1.21 g, 4.63 mmol), and dry hexane (35 ml) was refluxed for 1 day. The solution was filtered hot, the filtrate depositing more solid on cooling. After refiltration, the solid was vacuum sublimed at 50° to remove any unreacted $Mo(CO)_6$. The off-white solid decomposed without melting at >210°: ir (KBr) 960 (s), 926 (s), 808 (s–vs), 613 (s), and 573 cm^{-1} (m); nmr (DMSO-d_6) δ 1.08 (s), 1.36 (s), 1.48 (s), 1.56 (m).

Anal. Calcd for $C_{18}H_{36}Mo_3N_2O_2$: C, 36.04; H, 6.04; N, 4.66; Mo, 47.91; mol wt, 600. Found: C, 36.79; H, 6.00; N, 4.25; Mo, 47.50; mol wt, 618 (osmometry, $CHCl_3$).

Tungsten hexacarbonyl reacted with **1** to give a white solid having no melting point below 300°, ir (KBr) 979 (s), 958 (s, sh), 890 (w–m), 814 (vs), 448 cm^{-1} (m).

Anal. Calcd for $C_{18}H_{36}N_2O_2W_3$: C, 25.09; H, 4.20; N, 3.24; W, 63.83. Found: C, 25.76; H, 4.85; N, 3.21; W, 62.99.

2,2,6,6-Tetramethylpiperidine-1-oxyl was inert to $Cr(CO)_6$ under the reaction conditions used for $Mo(CO)_6$.

Registry No.—**1**, 2564-83-2; $Mo(CO)_6$, 13939-06-5; $C_{18}H_{36}Mo_3N_2O_2$, 37213-92-6; $W(CO)_6$, 14040-11-0; $C_{18}H_{36}N_2O_2W_3$, 37213-93-7.

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(14) Reference 8, p 217.
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A Mild, Nonacidic Method for Converting Secondary Nitro Compounds into Ketones

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The utility in synthesis of the mainfold transformations of nitroparaffins and nitro olefins[1] would be considerably enhanced if facile methods for converting nitro groups into carbonyl groups were at hand, and, indeed, there has recently been renewed interest in such transformations, especially as they relate to the synthesis of 1,4 diketones.[2,3] The purpose of this note is to describe a simple and effective method for converting secondary nitro compounds into ketones and diketones which does not use acids[4] or oxidizing[5] or reducing agents.[2] Its usefulness may be gauged from the data presented in Table I, especially if it is borne in mind that the yields of ketones and 1,4 diketones refer to pure, isolated products.

Our procedure derives from an observation reported in 1956 which appears to have been little, if at all, noticed, namely that 2-nitrooctane, while unaffected by

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(2) J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).
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(4) The Nef reaction [W. E. Noland, *Chem. Rev.*, **55**, 137 (1955)] involves the action of base to form the nitroparaffin salt which is then treated with a mineral acid. In the most recent paper[3] on the subject, 3 *N* hydrochloric acid is employed. The reductive procedure of McMurry and Melton[2] also involves acidic solutions.
(5) H. Shechter and F. T. Williams [*J. Org. Chem.*, **27**, 3699 (1962)] have described the permanganate oxidation of nitroparaffin salts to aldehydes and ketones.

TABLE I
THE CONVERSION OF SECONDARY NITRO COMPOUNDS INTO KETONES

Nitro compd[a]	Ketone[b]	Yield, %
2-Nitropropane	Acetone	70
2-Nitrooctane	2-Octanone	83
Nitrocyclohexane	Cyclohexanone	67
Nitrocycloheptane	Cycloheptanone	88
α-Phenylnitroethane	Acetophenone	79
5-Nitro-2-hexanone	2,5-Hexanedione	76
5-Nitro-2-octanone	2,5-Octanedione	71

[a] Registry numbers are, respectively, 79-46-9, 4609-91-0, 1122-60-7, 2562-40-5, 7214-61-1, 35223-72-4, and 7404-84-4. [b] Registry numbers are, respectively, 67-64-1, 111-13-7, 108-94-1, 502-42-1, 98-86-2, 110-13-4, and 3214-41-3.

nitrite esters and by sodium nitrite, is converted by their joint action into 2-octanone.[6] The overall reaction appears to be that of eq 1 and, consistent with this

$$R_2\underset{NO_2}{\underset{|}{C}}H + CH_3CH_2CH_2ONO + NaNO_2 \longrightarrow R_2C{=}O + CH_3CH_2CH_2OH + NaNO_3 + N_2O \quad (1)$$

view, nitrous oxide has been isolated and identified as one of the products. It should be emphasized that primary nitroparaffins on treatment with a nitrite ester and sodium nitrite give carboxylic acids and not aldehydes.[6]

As regards the mechanism of the reaction of eq 1, the sequence shown is suggested. Evidence for the first

$$R_2\underset{NO_2}{\underset{|}{C}}H + NO_2^- \rightleftarrows R_2\underset{NO_2}{\underset{|}{C}}^- + HNO_2 \quad (2)$$

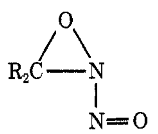
$$R_2\underset{NO_2}{\underset{|}{C}}^- + CH_3CH_2CH_2ONO \longrightarrow R_2\underset{NO_2}{\underset{|}{C}}NO + CH_3CH_2CH_2O^- \quad (3)$$

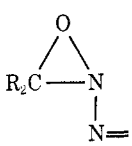
$$CH_3CH_2CH_2O^- + HONO \longrightarrow CH_3CH_2CH_2OH + NO_2^- \quad (4)$$

$$R_2\underset{NO_2}{\underset{|}{C}}NO + NO_2^- \longrightarrow R_2C{=}\ddot{N}O^- + N_2O_4 \quad (5)$$

$$R_2C{=}\ddot{N}O^- + O{=}NONO_2 \longrightarrow \left[R_2C{=}\underset{N=O}{\underset{|}{\overset{+}{N}}}O^- \longleftrightarrow R_2\overset{+}{C}\underset{N=O}{\underset{|}{\ddot{N}}}O^-\right] + NO_3^- \quad (6)$$

I

I ⟶  (7)

 $\longrightarrow R_2C{=}O + N_2O$ (8)

two steps of this sequence has already been presented.[6] The next step (eq 4) presents no difficulties. The reaction of eq 5 is a nucleophilic displacement on the nitro group of an α-nitroso nitro compound, a process which was recognized some years ago,[6,7] and in eq 6 nitrogen tetroxide is employed as a nitrosating agent, a role in keeping with the fact that one of the structures assigned to it is O=NONO$_2$.[8] The reaction of eq 6 is also consonant with the well-known transformation of oximes to aldehydes and ketones by the action of nitrous acid.[9] The last three steps (eq 6, 7, and 8) parallel those proposed by Wieland and Grim as a consequence of their study of the nitrous acid–ketoxime reaction using ^{18}O-enriched nitrous acid.[10] Finally, the fact that 2-nitroso-2-nitropropane is smoothly converted to acetone on treatment with sodium nitrite at room temperature accords with the proposed reaction scheme.[6]

Experimental Section

n-Propyl nitrite (bp 49–50°, n^{20}D 1.3592) and *n*-octyl nitrite (bp 50–52° at 4 mm, n^{20}D 1.4127) were prepared from the alcohols.[11,12] Nitroethane, 1-nitrobutane, and 2-nitropropane (Commercial Solvents) and nitrocyclohexane (Du Pont) were distilled prior to use. Nitrocycloheptane (bp 40–42° at 0.5 mm, n^{20}D 1.4723) was prepared from the bromide.[13]

α-Phenylnitroethane.[14]—Dry sodium nitrite (69 g, 1.0 mol) is dissolved in 800 ml of DMSO. The stirred solution is cooled to 19° and 92.4 g (0.50 mol) of α-phenylethyl bromide is added all at once. Stirring is continued and the internal temperature is maintained at 19–25° (minimal exposure to light). After 20 min the solution is poured into water layered with benzene; the benzene phase is washed with water, dried, and concentrated under reduced pressure. The resulting oil is dissolved in hexane and vigorously stirred with three 150-ml portions of 85% phosphoric acid, each treatment lasting 75 min (minimal light exposure). The hexane solution is then washed with water, dried over anhydrous magnesium sulfate, concentrated, and then twice distilled. This gives 38 g (50% yield) of vpc-pure α-phenylnitroethane, bp 61–63° at 0.45 mm, n^{20}D 1.5221.

5-Nitro-2-octanone.—A solution of freshly distilled methyl vinyl ketone (43.1 g, 0.617 mol), 1-nitrobutane (63.6 g, 0.617 mol), and diisopropylamine (31.2 g, 0.308 mol) in 300 ml of chloroform is refluxed for 15 hr and then concentrated under reduced pressure. Two distillations of the residual oil give 74.6 g (70% yield) of vpc-pure, colorless 5-nitro-2-octanone, bp 72° at 0.45 mm, n^{20}D 1.4428 (lit.[15] n^{20}D 1.4414–1.4428).

5-Nitro-2-hexanone.—Methyl vinyl ketone and nitroethane were condensed exactly as above to give a 44% yield of 5-nitro-2-hexanone, bp 72–73° at 0.95 mm, n^{20}D 1.4401 (lit.[16] $n^{19.6}$D 1.4396).

Conversion of Nitro Compounds into Ketones. α-Phenylnitroethane into Acetophenone.—Under nitrogen 34.5 g (0.50 mol) of dry sodium nitrite is added to 200 ml of DMSO and this is followed by 15.12 g (0.10 mol) of α-phenylnitroethane and 17.82 g (0.20 mol) of *n*-propyl nitrite. The resulting mixture is stirred for 2 hr, in subdued light, at 23–28° (occasional cooling), after which it is poured into water layered with methylene chloride. The methylene chloride phase is separated, washed with water, and dried over anhydrous magnesium sulfate, and then the methylene chloride is removed. Distillation of the residual oil at 6 mm gives 9.45 g (79% yield) of pure acetophenone, bp 66–67°, n^{20}D 1.5341.

Nitrocycloheptane into Cycloheptanone.—Nitrocycloheptane (21.48 g, 0.15 mol), sodium nitrite (51.75 g, 0.75 mol), *n*-propyl nitrite (26.73 g, 0.30 mol), and 300 ml of DMSO are employed as above (reaction time 5 hr). This gives 14.78 g (88% yield of vpc-pure cycloheptanone, bp 50–52° at 6 mm, n^{20}D 1.4615.

Nitrocyclohexane into Cyclohexanone.—Nitrocyclohexane (18.91 g, 0.15 mol) is treated with sodium nitrite and *n*-propyl

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(16) H. Shechter, D. L. Ley, and L. Zeldin, *J. Amer. Chem. Soc.*, **74**, 3664 (1952).

nitrite as above for 50 hr. Vpc-pure cyclohexanone is obtained in 67% yield (9.75 g), bp 154–155°, n^{20}D 1.4505.

5-Nitro-2-hexanone into 2,5-hexanedione.—The nitro ketone (21.78 g, 0.15 mol), sodium nitrite (51.75 g, 0.75 mol), *n*-propyl nitrite (26.73 g, 0.30 mol), and 300 ml of DMSO are employed as above (reaction time 20 hr). Since the dione is water soluble, relatively large amounts of methylene chloride and relatively small amounts of water are used in the work-up. Also, the crude dione is chromatographed on silica gel prior to distillation. There is obtained 13.25 g (76% yield) of vpc-pure 2,5-hexanedione, bp 58–60° at 5 mm, n^{20}D 1.4253. The nmr spectrum consists of a singlet at δ 2.1 (6 H) and a singlet at 2.6 (4 H).

5-Nitro-2-octanone into 2,5-Octanedione.—Using 25.97 g (0.15 mol) of this nitro ketone the reaction is carried out as in the preceding experiment (reaction time 52 hr). The vpc-pure dione (bp 44–45° at 0.47 mm) is obtained in 71% yield (15.13 g), n^{20}D 1.4313 (lit.[17] n^{23}D 1.4317).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.49; H, 10.14.

2-Nitropropane into Acetone.—To facilitate isolation of the product hexamethylphosphoramide (HMPA) was employed as the solvent and *n*-octyl nitrite as the nitrosating agent. Under nitrogen, a mixture of 55.20 g (0.80 mol) of dry sodium nitrite, 35.99 g (0.40 mol) of 2-nitropropane, and 79.61 g (0.50 mol) of *n*-octyl nitrite in 800 ml of HMPA is stirred at 25–28° (subdued light) for 4.5 hr. The acetone is removed directly from the reaction mixture at room temperature *in vacuo* and collected at −80°. Distillation from Drierite gives 16.10 g (70% yield) of pure acetone, bp 56–58°, n^{20}D 1.3588.

Identification of Nitrous Oxide.—A colorless gas is evolved in all of these transformations. A sample of the gas produced in the conversion of 2-nitropropane to acetone (*vide supra*) was collected after passing through a −80° trap. Mass spectroscopy reveals, in addition to N_2 and O_2 peaks at *m/e* 28 and 32, peaks at *m/e* 44 (100%) for N_2O and *m/e* 30 (40%) presumed to be NO^+ derived from N_2O. A high resolution peak to peak comparison of the *m/e* 44 peak with the *m/e* 44 peak of CO_2 confirms the presence of nitrous oxide.[18] Calcd for N_2O: *m/e* 44.0011. Found: *m/e* 44.0003.

Registry No.—Sodium nitrite, 7632-00-00; α-phenylethyl bromide, 585-71-7.

Acknowledgment.—We thank the National Science Foundation and Eli Lilly and Co. for generous support.

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(18) We are indebted to Mr. W. Perry of the Purdue Mass Spectrometry Center for determining these spectra.

Datiscacin, a Novel Cytotoxic Cucurbitacin 20-Acetate from *Datisca glomerata*[1a,b]

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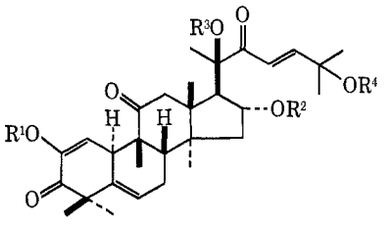
In the course of a continuing search for tumor inhibitors of plant origin, a chloroform extract of *Datisca glomerata* Baill. (Cucurbitaceae) was found to show significant activity against human carcinoma of the nasopharynx (KB) carried in cell culture.[2] A number of tumor-inhibitory principles have been isolated from this plant and the structure elucidation of one of these, datiscoside, has already been reported.[3] We report herein the structure elucidation of another cytotoxic principle, datiscacin (**1**), the first recognized cucurbitacin 20-acetate ester derivative.

The chloroform extract of the dried roots was subjected to successive solvent partitions and chromatographic separations, guided by the KB assay. Datiscacin[4] (**1**), $C_{32}H_{44}O_8$, mp 208–212°, $[\alpha]^{23}$D −18°, was crystallized from a cytotoxic fraction.

Elemental analysis and spectral data for datiscacin supported its formulation as a cucurbitacin monoacetate ester. Acetylation of datiscacin under mild conditions with acetic anhydride–pyridine yielded a triacetate (**2**), indicative of the location of the original acetate group on the C-17 side chain. That datiscacin contains a diosphenol in ring A was indicated by its positive ferric chloride test, absorption at 6.13 μ in the infrared and 268 nm in the ultraviolet, a one-proton doublet at τ 4.29 in the nmr spectrum,[5] and a peak at *m/e* 164 in the mass spectrum.[6] The known cucurbitacin E (**3**) contains a ring A diosphenol and a C-25 acetate ester, but its markedly different optical rotation ($[\alpha]^{26}$D −58°)[7] indicated that it differed from datiscacin. These considerations and the fact that there are but two hydroxyl groups in the cucurbitacin side chain led us to entertain the hypothesis that datiscacin is the C-20 acetate ester **1**.



1, $R^1 = R^2 = R^4 = H$; $R^3 = Ac$
2, $R^1 = R^2 = R^3 = Ac$; $R^4 = H$
3, $R^1 = R^2 = R^3 = H$; $R^4 = Ac$
4, $R^1 = R^2 = R^3 = R^4 = H$
5, $R^1 = R^2 = Ac$; $R^3 = R^4 = H$

Confirmation for the position of the acetate ester in **1** was derived from the results of periodate oxidation studies. Thus, datiscacin diacetate (**2**) was found to be unaffected by treatment with an excess of periodic acid, and the compound was recovered unchanged. In contrast, treatment of cucurbitacin I diacetate (**5**)[8] with periodic acid under the same conditions led to consumption of 1 molar equiv of the reagent, in accord with the expected sensitivity of the 20,22-ketol system.

Interrelation with a known cucurbitacin was deemed desirable to confirm the postulated structure and configuration of datiscacin. Hydrolysis of the tertiary C-20 acetate ester group to yield cucurbitacin I (**4**) was envisaged, but strong alkaline treatment was precluded by the known sensitivity of ring A diosphenols

(1) (a) Tumor Inhibitors. LXXXIII. Part LXXXII: S. M. Kupchan, R. W. Britton, M. F. Ziegler, and C. W. Sigel, *J. Org. Chem.* **38**, 178 (1973). (b) This investigation was supported by grants from the National Cancer Institute (CA-11718) and the American Cancer Society (IC-57H), and a contract with the National Cancer Institute (NIH-NCI-C-71-2099). (c) National Institutes of Health Postdoctoral Fellow, 1972–present.

(2) Cytotoxicity was assayed, under the auspices of the National Cancer Institute, by the procedure described in *Cancer Chemother. Rep.*, **25**, 1 (1962).

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(4) Datiscacin showed significant cytotoxicity (ED_{50} = 2.9 × 10^{-2} μg/ml) against cells derived from the human carcinoma of the nasopharynx (KB).

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