(*b*) *Alcoholysis.* Twenty to thirty ml. of the alcohol were treated with 0.1 g. of sodium. When reaction was completed, one gram of methyl 2-phenothiazinecarboxylate was added, and the mixture was refluxed 4–5 hr. The mixture was poured into water, filtered, dried, and recrystallized from ethanol-acetone mixtures.

Acknowledgment. We wish to thank the National Cancer Institute, grant CY-2450-3 and the Upjohn Drug Co. for financial assistance, the Upjohn Drug Co. (Dr. R. F. Heinzelmann) for analyses, Dr. C. C. Stock (Sloan Kettering Institute) and Dr. R. H. Levin (The Upjohn Drug Co.) for physiological testing.

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A New Technique in Preparing 2,4-Dinitrophenylhydrazones. Use of Diglyme as Solvent

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Received August 22, 1958

An encumberance long associated with the characterization of carbonyl compounds by their 2,4-dinitrophenylhydrazones is the difficulty of obtaining concentrated solutions of 2,4-dinitrophenylhydrazine. The low solubility of the reagent in useful solvents is usually overcome by working with boiling solvents or with highly acidic solutions, since the salts of the reagent are more soluble than the reagent itself. Thus, 2,4-dinitrophenylhydrazones are usually prepared by resorting to one of several techniques now in practice. These are, for example, adding to the carbonyl compound a solution of the reagent in concentrated sulfuric acid, water, and ethanol[1]: adding a solution of the reagent in ethanol containing hydrochloric acid[2]; adding a solution of the reagent in 85% phosphoric acid and ethanol[3]; boiling the carbonyl compound in a methanol solution of the reagent acidified with hydrochloric acid[4]; boiling the carbonyl compound, reagent, and hydrochloric acid in ethanol[5]; uniting the carbonyl compound, reagent and hydrochloric acid in a mixture of ethanol and dioxane[6]; and adding an alcoholic solution of the carbonyl compound to a saturated solution of the reagent in $2M$ hydrochloric acid.[7]

It has now been found that 2,4-dinitrophenylhydrazine is quite soluble in the dimethyl ether of diethylene glycol, for which solvent the name diglyme has been coined.[8] Solutions of the reagent made by warming 1 g. in 25 to 30 ml. of the solvent are stable at room temperature. The neutral solution is deep red in color. Acidification with hydrochloric acid turns the color to yellow. It is not necessary to acidify the reagent solution for storage, however. Solutions of the reagent in diglyme have been found to be admirable for the preparation of derivatives, using, as is customary, hydrochloric acid for catalysis.

Moderate success was also achieved in the use of acetic acid instead of hydrochloric acid for catalysis. The reason for using acetic acid was two-fold. The use of a weak acid for catalysis in solutions at room temperature or lower may be applicable to the preparation of derivatives of sensitive compounds. Also, in the preparation of derivatives of carbonyl compounds formed in the oxidation of glycols by lead tetraacetate the precipitation of the derivative may be complicated by the precipitation of lead chloride, unless the trouble is taken first to separate the carbonyl compounds from lead acetate. If acetic acid can be used for catalysis of 2,4-dinitrophenylhydrazone formation it may be possible to use crude oxidation mixtures in the preparation of derivatives. Results with lead tetraacetate oxidation solutions will be published elsewhere. As can be seen in Table I success was achieved in the four cases tried. However, the formation of the derivatives was slow. In the case of benzaldehyde the derivative crystallized nicely from solution 30 min. after adding the acetic acid. In the cases of methyl *p*-tolyl ketone and 7-ethyl-1-tetralone the derivatives crystallized out overnight. In each case, however, the amount of derivative obtained was much smaller than expected from the amount of compound used. The use of solutions of 2,4-dinitrophenylhydrazine in acetic acid alone or in aqueous acetic acid is to be avoided since acetylation of the reagent occurs when warming to dissolve. No acetylation occurred in a control diglyme experiment.

As might be expected, triglyme[8] and tetrahydrofuran can be used as solvents for 2,4-dinitrophenylhydrazine. Undoubtedly, other solvents may be found. Because tetrahydrofuran needs to be distilled prior to use and because of its volatility, we found diglyme to be preferred. It was found unnecessary to distill the diglyme before use.

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EXPERIMENTAL

The following procedure was used, in general, in preparing the derivatives given in Table I.

TABLE I

Melting Points[a] and Literature Values

Compound	M.P.	Lit., °C.
methyl *n*-hexyl ketone[b]	58–59	58[k]
methyl isobutyl ketone[b]	92–93[h]	95[k]
methyl isopropyl ketone[b]	123–124	117[k], 119–120[m]
acetone[b]	125–126	126[k]
acetone[b,e]	124–126	126[k]
cyclohexanone[c]	160–161	161[k]
acetaldehyde[b]	165–166[i]	168[k]
formaldehyde[b]	165–166	166[k]
benzaldehyde[d]	238–240	237[k]
benzaldehyde[c,e]	239–240	237[k]
benzaldehyde[d,f]	239–240	237[k]
benzaldehyde[d,g]	239–240	237[k]
acetophenone[d]	247–248	250[k]
cinnamaldehyde[d]	255–256	255[k]
methyl *p*-tolyl ketone[d]	257–259[j]	260[k]
methyl *p*-tolyl ketone[c,e]	247–254	260[k]
7-ethyltetralone-1[d]	271–272	275[n]
7-ethyltetralone-1[c,e]	273–274	275[n]
p-hydroxybenzaldehyde[d]	284–284.5	280[k]

[a] Uncorrected. [b] Dilution with water needed to precipitate derivative. [c] Derivative crystallized out slowly. [d] Derivative precipitated immediately on adding acid. [e] Ten drops of acetic acid used instead of hydrochloric acid. [f] Triglyme solution of reagent. [g] Tetrahydrofuran solution of reagent. [h] Recrystallized from ethanol: m.p. before was 86–89°. [i] Recrystallized from ethanol; m.p. before was 153–154°. See ref. 4, p. 586. [j] Recrystallized from diglyme: m.p. before was 249–256°. [k] Ref. 1. [m] Ref. 4. [n] This was prepared in these laboratories by a conventional technique and recrystallized from ethyl acetate. Calcd. for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12; N, 15.80. Found[9]: C, 61.21; H, 5.19; N, 15.51.

A solution of 4 g. of 2,4-dinitrophenylhydrazine was prepared by warming in 120 ml. of diglyme and allowed to stand at room temperature for several days. Five ml. of this solution, at room temperature, was added to approximately 0.1 g. of the carbonyl compound dissolved in 1 ml. of 95% ethanol. Where the carbonyl compound was insoluble in 95% ethanol it was dissolved in diglyme, as, for example, in the case of *p*-hydroxybenzaldehyde. Three drops of concentrate hydrochloric acid were then added, causing the immediate formation of the derivative. In some cases the derivative precipitated immediately, in others dilution with water was necessary, while in one the derivative crystallized out slowly. The derivative was filtered, washed with ethanol or aqueous ethanol and dried by suction. In only three cases was it necessary to recrystallize the derivative to obtain a satisfactory melting point. Thus, the new technique gave *excellent crudes* in most cases, within a few minutes work.

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Oxidation of Methyl 8-Nitrodehydroabietate. II[1]

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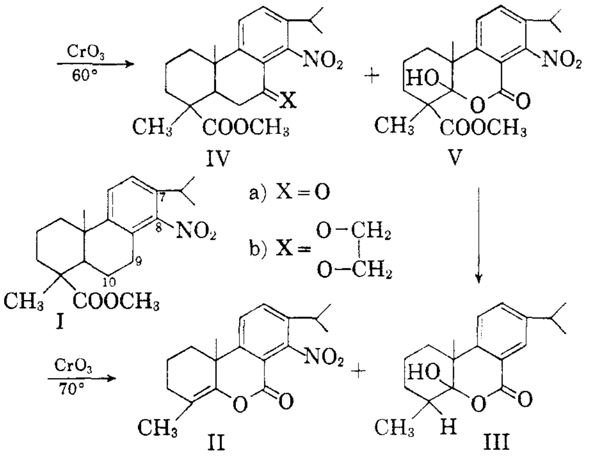
Received August 25, 1958

We wish to report the results of a study of the oxidation of methyl 8-nitrodehydroabietate I with chromium trioxide at 60°. The oxidation of I with this trioxide at 70° has been shown to involve the destruction of the hydrophenanthrene system, and the products of the oxidation have been formulated as the ketol lactone III and the enol lactone II arising from III by dehydration.[1] It has now been found possible to isolate compounds IVa and V from oxidations at 60° as intermediates in the formation of the ketol lactone III.

The neutral fraction of the oxidation mixture in the present work consists of methyl 9-oxo-8-nitrodehydroabietate IVa and is characterized by way of its 2,4-dinitrophenylhydrazone and ethylene ketal derivatives. The ultraviolet spectrum of IVa is consistent with this formulation, since the conjugation of the carbonyl function at C-9 with the phenyl ring causes a shift in the positions of the absorption maxima of methyl 8-nitrodehydroabietate I as well as a large increase in the intensity of absorption (see Table I). Formation of the ethylene ketal IVb blocks this conjugation and its spectrum is very similar to that of I, although a small bathochromic shift is noticed in this case owing to the presence of the polar ketal group. The infrared spectrum (Table I) of the ketone IVa also shows the presence of the conjugated ketonic system by an absorption band at 5.91μ.

Figure I



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[1] Paper I: H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **77**, 6707 (1955).

[2] Felton Chemical Co., Inc., 599 Johnson Ave., Brooklyn 37, N. Y.