TABLE I

2-HYDROXY-3-R-QUINOXALINES

R	M.p., °C.	Yield, %	Solvent	Appearance	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$—CH_2CO_2C_2H_5$	204–205	85	Alcohol	Yellow	...	...	..	..	12.06	12.18
$—CH(CH_3)CO_2C_2H_5$	160	95	Alcohol	Colorless	...	...	..	..	11.38	11.45
$—CH(CH_2)_2CH_2$ └—CO—┘	256–258 dec.	90	Alcohol	Dark red	68.42	68.31	5.30	5.32	12.28	12.30
$—CH(CH_2)_2CHCOCO_2Et$ └—CO—┘	>360	70	Pyridine	Dark purple	62.18	62.08	4.91	5.12	8.54	8.70

low *p*H, and the prevailing high dilution. In general, however, quinoxalinols are formed rapidly and in almost quantitative yields and thus provide the best available derivatives of α-keto esters.

Experimental

General Procedure.—Equimolar proportions of α-keto ester and *o*-phenylenediamine were refluxed in alcoholic solution (with or without added glacial acetic acid) for several hours. Ten minutes heating sufficed in the cases of less soluble quinoxalinols. The products were isolated by filtration or evaporation, followed by recrystallization. The data are collected in Table I.

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The Displacement of Positive Halogen from Tri-(*p*-nitrophenyl)-methyl Halides[1]

BY M. FREDERICK HAWTHORNE

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During the course of an investigation of the chemistry of tri-(*p*-nitrophenyl)-methyl nitrate[2] it was observed that the treatment of this nitrate ester with iodide ion in acetone solution produced the green tri-(*p*-nitrophenyl)-methyl radical and iodine. This reaction was similar to that reported by Leffler[3] for the corresponding bromide and both reactions were examined in greater detail.

One of the possible paths for the production of the triarylmethyl radical from triarylmethyl bromide and iodide ion is the nucleophilic displacement of "positive" bromine by iodide ion to produce the tri-(*p*-nitrophenyl)-methide ion which, in turn, may be oxidized by the liberated halogen to the free radical. Alternatively, the reaction could take the course of a nucleophilic attack on carbon by iodide ion followed by the spontaneous homolytic dissociation of the resulting triarylmethyl iodide.

$$R_3CBr + I^{\ominus} \longrightarrow R_3C^{\ominus} + IBr \longrightarrow R_3C\cdot + I\cdot + Br^{\ominus}$$
$$R = p\text{-nitrophenyl}$$

The production of triarylmethyl radical from the nitrate ester, under identical circumstances, could proceed through the agency of the similar reaction sequence

$$R_3CONO_2 + I^{\ominus} \longrightarrow R_3CI + NO_3^{\ominus}$$
$$R_3CI + I^{\ominus} \longrightarrow R_3C^{\ominus} + I_2 \longrightarrow R_3C\cdot + I\cdot + I^{\ominus}$$

or

$$R_3CI \longrightarrow R_3C\cdot + I\cdot$$
$$R = p\text{-nitrophenyl}$$

In order to choose from among the numerous possible mechanisms for these reactions (nucleophilic attack on carbon *versus* nucleophilic attack on halogen) the reactions of triarylmethyl bromide and nitrate with iodide ion were examined in acetic acid–methylene chloride. In this medium the nucleophilic attack of iodide ion on halogen should still occur, with the liberation of iodine, as in acetone solution but the resulting triarylmethide ion intermediate should be effectively captured as hydrocarbon due to the presence of a proton donor and little radical should result. This reaction path was indicated to be correct by the isolation of high yields of tri-(*p*-nitrophenyl)-methane, iodine and some carbinol from the reaction of the bromide and nitrate esters with iodide ion under these conditions. A similar experiment conducted by Leffler[3] was unsuccessful due to the relatively low concentration of acetic acid employed. The nitrate ester produced a small amount of triarylmethyl radical and this is attributed to the homolytic dissociation of the intermediate iodide. The presence of carbinol among the reaction products is explained on the basis of acetolysis of the triarylmethyl nitrate or iodide followed by hydrolysis of the resulting acetate during chromatography on alumina. A control experiment showed that tri-(*p*-nitrophenyl)-methyl is not reduced by iodide ion to the methide ion.

Experimental

The Reaction of Tri-(*p*-nitrophenyl)-methyl Nitrate with Iodide Ion in Acetic Acid–Methylene Chloride.—Two grams (0.0044 mole) of tri-(*p*-nitrophenyl)-methyl nitrate, prepared as previously described,[2] was dissolved in 200 ml. of 50–50 (volume) acetic acid–methylene chloride and 3.50 g. of sodium iodide quickly added. Iodine was immediately released and the solution was allowed to stand at room temperature for one hour and then quickly filtered to remove a small amount of green triarylmethyl radical (0.38 g., weighed as peroxide, m.p. 212–214°). The filtrate was flooded with water, washed with excess sodium thiosulfate solution, washed again with water and the organic layer dried over magnesium sulfate. Evaporation of the solution to dryness produced an orange solid which was dissolved in a minimum of 50–50 benzene–methylene chloride and placed on a 15-cm. non-alkaline, activity grade I alumina column. The column was eluted with methylene chloride to produce 0.97 g. (0.0026 mole) of pure tri-(*p*-nitrophenyl)-methane (m.p. 210–212°, base soluble with blue coloration) followed by 0.25 g. (0.00065 mole) of tri-(*p*-nitrophenyl)-carbinol (m.p. 180–183° after one recrystallization from ethanol–water).

In order to prove that tri-(*p*-nitrophenyl)-methyl is not reduced by iodide ion under the above reaction conditions, 1.00 g. of freshly prepared radical was treated with 5.0 g. of sodium iodide in 50 ml., of reaction solvent. The green radical persisted for at least several hours.

The Reaction of Tri-(*p*-nitrophenyl)-methyl Bromide with Iodide Ion in Acetic Acid–Methylene Chloride.—This experiment was conducted in exactly the same manner as that of the nitrate ester except that 2.80 g. of bromide (0.0079 mole) was used with 4.0 g. of sodium iodide. No free radical was obtained, but 1.56 g. (0.0043 mole) of the tri-(*p*-

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) M. F. Hawthorne, THIS JOURNAL, **77**, 5523 (1955).

(3) J. E. Leffler, *ibid.*, **75**, 3598 (1953).

nitrophenyl)-methane and 0.43 g. (0.0011 mole) of tri-(*p*-nitrophenyl)-carbinol were separated from the reaction products.

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Selective Reduction of Aliphatic Nitroesters with Lithium Aluminum Hydride[1]

BY HENRY FEUER AND THOMAS J. KUCERA

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The selective reduction of ethyl *p*-nitrobenzoate and ethyl *p*-nitrophenylacetate to the corresponding nitroalcohols with lithium aluminum hydride at 25° has been reported by Felkin.[2] We wish to report the successful reduction of aliphatic nitroesters, containing a secondary, tertiary or *gem*-dinitro group, to the corresponding nitrocarbinols in yields which compare favorably with those obtained by the reduction of aliphatic nitroaldehydes with sodium borohydride.[3] The reductions were carried out smoothly at −30 to −60° by employing a slight excess of the hydride and ether as the solvent, except in the case of dimethyl 4,4-dinitropimelate where tetrahydrofuran had to be used because of the limited solubility of this ester in ether at low temperatures.

Since methyl 4-nitropentanoate did not evolve hydrogen when treated with the hydride at low temperatures, several nitroesters with more highly active hydrogens were tested. It was found that ethyl 2-nitropropanoate, ethyl 2-nitrocaproate and ethyl 3-nitropropanoate reacted with lithium aluminum hydride at −30 to −60° without the evolution of hydrogen. However, great difficulty was encountered in the isolation of the alcohols because of the high water solubility of the nitropropanols[4] and known tendency of the 2-nitro-1-hexanol to dehydrate to the olefin upon distillation.[5]

TABLE I

Methyl ester	Product	Yield, %
4-Nitropentanoate	4-Nitropentanol	61[e]
4-Methyl-4-nitropentanoate[a]	4-Methyl-4-nitropentanol[d]	76[e]
4,4-Dinitropentanoate[b]	4,4-Dinitropentanol[d]	53
4,4-Dinitropimelate[c]	4,4-Dinitro-1,7-heptanediol	56

[a] H. A. Bruson, U. S. Patent 2,342,119 (1949). [b] H. Shechter and L. Zeldin, THIS JOURNAL, **73**, 1276 (1951). [c] L. Herzog, *et al.*, *ibid*, **73**, 749 (1951). [d] Identified by physical properties and derivatives according to H. Shechter, *et al.* (ref. 3). [e] Some of the starting ester was recovered.

Experimental[6]

The following procedure is representative of the preparation of the various nitroalcohols.

4-Nitropentanol.—Methyl 4-nitropentanoate[7] (13.87 g., 86 mmoles) was dissolved in 60 ml. of anhydrous ether and the solution cooled to −35°. Lithium aluminum hydride solution in ether (53.7 ml. of 0.81 *M*, 43 mmole) was added dropwise over a 15-minute period and the solution was stirred for another 20 minutes before 5 ml. of ethyl acetate was added. Hydrolysis was then carried out at 0° with 50 ml. of 20% phosphoric acid with 6 g. of urea dissolved in it. The layers were separated and the aqueous layer extracted with two 50-ml. portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate and the solvent was removed by distillation. The residue was distilled to yield 0.67 g. of the starting ester, b.p. 90–94° at 2 mm. and 4-nitropentanol (6.67 g., 61% conversion), b.p. 90–92° at 1 mm., $n^{20}\text{D}$ 1.4479; lit. value[3] b.p. 91–92.5° at 1 mm., $n^{20}\text{D}$ 1.4475. The alcohol was converted in a Nef[8] reaction to 5-hydroxy-2-pentanone and the ketone was characterized by its 2,4-dinitrophenylhydrazone, m.p. 146–147°; lit. value[3] m.p. 146–147°.

4,4-Dinitro-1,7-heptanediol.—The same experimental procedure was followed as above except that tetrahydrofuran was employed as the solvent. The diol was obtained as a white solid, m.p. 74.5–75° after recrystallization from methylene chloride.

Anal. Calcd. for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.35; N, 12.61. Found: C, 37.92; H, 6.56; N, 12.88.

The bis-phenylurethan, m.p. 119.5–120°, was prepared and recrystallized from ethylene chloride.

Anal. Calcd. for $C_{21}H_{24}N_4O_8$: C, 54.78; H, 5.25; N, 12.17. Found: C, 55.50; H, 5.40; N, 12.43.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

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[1] From the Ph.D. thesis of Thomas J. Kucera, Purdue University, 1953.

[2] H. Felkin, *Compt. rend.*, **230**, 305 (1950).

[3] H. Shechter, D. E. Ley and L. Zeldin, THIS JOURNAL, **74**, 3664 (1952).

[4] "Nitrohydroxy Derivatives of the Nitroparaffins," Commercial Solvents Corp., New York, N. Y.

[5] E. F. Degering and R. Hoaglin, *Proc. Indiana Acad. Sci.*, **52**, 119 (1942).

[6] All melting points are uncorrected.

[7] H. Bruson, U. S. Patent 2,390,918 (1945).

[8] J. U. Nef, *Ann.*, **280**, 263 (1894).

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The Reactions of Triphenylgermyllithium with Formaldehyde and with Benzophenone

BY HENRY GILMAN AND CLARE W. GEROW

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It has been reported[1] previously that triphenylsilylpotassium reacts with formaldehyde in diethyl ether to form, along with other unidentified material, triphenylhydroxymethylsilane (I). The same authors report[2] that triphenylsilylpotassium

$$(C_6H_5)_3SiK + HCHO \xrightarrow{H_2O} \underset{\text{I}}{(C_6H_5)_3SiCH_2OH}$$

reacts with benzophenone in diethyl ether to give benzohydryloxytriphenylsilane (II). In the former

$$(C_6H_5)_3SiK + (C_6H_5)_2CO \xrightarrow{H_2O} \underset{\text{II}}{(C_6H_5)_3SiOCH(C_6H_5)_2}$$

reaction the triphenylsilylpotassium adds to the carbonyl group in such a manner that in the product I the silicon atom is attached to the carbon atom of the carbonyl group. In the latter reaction the product II has the silicon atom attached to the oxygen atom of the carbonyl group.

We have found that triphenylgermyllithium adds to formaldehyde in ethylene glycol dimethyl ether in the same manner as triphenylsilylpotassium to give triphenylhydroxymethylgermane.

$$(C_6H_5)_3GeLi + HCHO \xrightarrow{H_2O} \underset{\text{III}}{(C_6H_5)_3GeCH_2OH}$$

However, we have also established that triphenylgermyllithium reacts with benzophenone in ethylene

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[1] H. Gilman and T. C. Wu, THIS JOURNAL, **76**, 2502 (1954).

[2] H. Gilman and T. C. Wu, *ibid.*, **75**, 2935 (1953).