homogeneity the solution was concentrated to dryness. The concentrate was dissolved in ethanol, and the aldehyde was converted to its 2,4-dinitrophenylhydrazone. After two crystallizations, the m.p.'s of the derivatives so prepared were 211–212°. The ketone IIab and the derivative of the aldehyde IIIa reisolated from each reaction mixture then were assayed for radioactivity. The results of these assays are given in Table VI. From these data, the yields, in mg. of II and III, may be calculated as

$$\frac{x}{x + 500}(2.032) = \text{assay of IIab}$$

$$\frac{y}{y + 500}(2.032) = \text{assay of IIIa 2,4-DNPH}$$

where x = yield of ketone II and y = yield of aldehyde III. From calculations of the foregoing type, were obtained the results given in Table II.

Anal. Calcd. for $C_{26}H_{20}N_4O_4$: C, 69.03; H, 4.42; N, 12.40. Found: C, 69.06, 68.92; H, 4.46, 4.59; N, 12.73, 12.94.

Radioactivity Determinations.—These were carried out as previously described, using the Van Slyke wet combustion method in conjunction with ion-current measurements of the evolved carbon-C^{14} dioxide using a vibrating reed electrometer.[2] The uncertainties expressed for radioactivity assays are average deviations from the mean value of two or more determinations.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Thermal Decomposition of Tri-(*p*-nitrophenyl)-methyl Nitrate. A New Example of the Wieland Rearrangement[1]

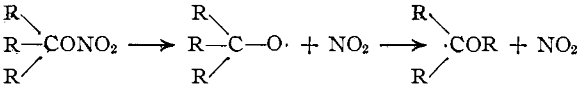
BY M. FREDERICK HAWTHORNE

RECEIVED MAY 31, 1955

Tri-(*p*-nitrophenyl)-methyl nitrate has been prepared, characterized and found to be relatively stable toward solvolytic decomposition. The thermal decomposition of tri-(*p*-nitrophenyl)-methyl nitrate, when carried out in the absence of air and in chlorobenzene solution at 130°, produces 4,4′-dinitrobenzophenone, 2,4-dinitrophenol, tri-(*p*-nitrophenyl)-carbinol and a moderate yield of 4,4′,4″,4‴-tetranitrobenzpinacol di-(*p*-nitrophenyl)-ether, the dimer resulting from the Wieland rearrangement of the tri-(*p*-nitrophenyl)-methoxy radical.

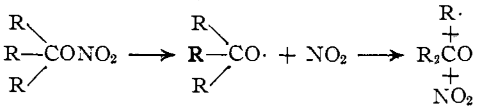
The recent preparation of triphenylmethyl nitrate[2–4] has shown this compound to be an extremely unstable entity which decomposes on attempted isolation. Baker and Heggs[5] have reported the isolation and characterization of a similarly reactive nitrate ester, benzhydryl nitrate. Both of these esters are characterized by extremely facile solvolytic reactions, as shown by the production of N-diphenylmethylacetamide from the reaction of benzhydryl nitrate with acetamide at 80–120°.

Perhaps the most interesting feature of this class of nitrate ester is their potential ability to undergo the Wieland[6] rearrangement (1) upon homolytic thermal decomposition. Cristol and Leffler[2] have reported that the thermal decomposition of triphenylmethyl nitrate in such solvents as carbon tetrachloride and nitrobenzene yields triphenylcarbinol, benzophenone, picric acid and oxides of nitrogen. These products were rationalized by the authors on the basis of a β-cleavage process (2) followed by a series of oxidation–reduction reactions which lead eventually to picric acid. No direct evidence for the process 1 was obtained.



$$\mathrm{R_3CONO_2 \longrightarrow R_3C{-}O\cdot + NO_2 \longrightarrow R_2\cdot COR + NO_2}$$

R = aryl group (1)



$$\mathrm{R_3CONO_2 \longrightarrow R_3CO\cdot + NO_2 \longrightarrow R\cdot + R_2CO + NO_2} \quad (2)$$

R = phenyl

In view of these results it was of importance to prepare a stable triarylmethyl nitrate ester which might illustrate a Wieland rearrangement. Since Bartlett and Cotman[7] have shown that diphenyl-(*p*-nitrophenyl)-methyl hydroperoxide gives nearly exclusive migration of the *p*-nitrophenyl group on thermal decomposition, one would expect tri-(*p*-nitrophenyl)-methyl nitrate (I) to be quite favorably constituted to give a similar rearrangement on thermal decomposition. Furthermore, the introduction of *p*-nitro groups into trityl nitrate should increase the solvolytic stability of the resulting nitrate ester.

Tri-(*p*-nitrophenyl)-methyl nitrate (I) was prepared in high yields by the metathetical reaction of silver nitrate with tri-(*p*-nitrophenyl)-methyl bromide in acetonitrile at room temperature. The material proved to be unusually stable toward solvolytic hydrolysis but gave oxides of nitrogen on long standing in the crystalline state or on melting (156°).

When compound I was treated with iodide ion in acetone solution, the intensely green color of the tri-(*p*-nitrophenyl)-methyl radical was observed in the presence of iodine.[8]

Solution of (I) in concentrated sulfuric acid resulted in the formation of the orange tri-(*p*-nitrophenyl)-methylcarbonium ion and not an ion similar to the light yellow oxonium ion resulting from the protonation of *p,p*′-dinitrobenzophenone. The nitrate ester I is apparently cleaved according to path 3 in preference to 4.[9]

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

[2] S. J. Cristol and J. E. Leffler, THIS JOURNAL, **76**, 4468 (1954).

[3] R. T. Merrow and R. H. Boschan, *ibid.*, **76**, 4622 (1954).

[4] G. W. Cheeseman, *Chemistry and Industry*, 281 (1954).

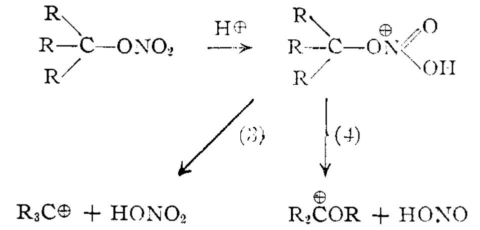
[5] J. W. Baker and T. G. Heggs, *ibid.*, 464 (1954).

[6] H. Wieland, *Ber.*, **44**, 2550 (1911).

[7] P. D. Bartlett and J. D. Cotman, THIS JOURNAL, **72**, 3095 (1950).

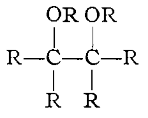
[8] J. E. Leffler, *ibid.*, **75**, 3598 (1953), reported many examples of similar reactions involving tri-(*p*-nitrophenyl)-methyl bromide.

[9] Path 4 represents the acid-catalyzed decomposition of the nitrate ester by a path similar to that observed in the acid-catalyzed decomposition of certain tertiary hydroperoxides. See reference 7 for an example of this hydroperoxide rearrangement. Evidently the low ionic migratory aptitude of the *p*-nitrophenyl group makes this path quite unfavorable.



R = *p*-nitrophenyl

The thermal decomposition of I was carried out in chlorobenzene solution at 120–130° and in the absence of air. Under these conditions nitric oxide was evolved (as shown by its ferrous ion complex) and no nitrogen dioxide was detected. A chromatographic examination of the reaction mixtures revealed the presence of 2,4-dinitrophenol, 4,4'-dinitrobenzophenone, tri-(*p*-nitrophenyl)-carbinol, a moderate amount of a new compound II melting at 288–289° and some highly colored unidentified material. The compound II was found to produce *p*-nitrophenol when heated under reflux with sodium hydroxide in ethylene glycol or aqueous dioxane and to have infrared spectral characteristics and an elemental analysis compatible with the benzpinacol structure.

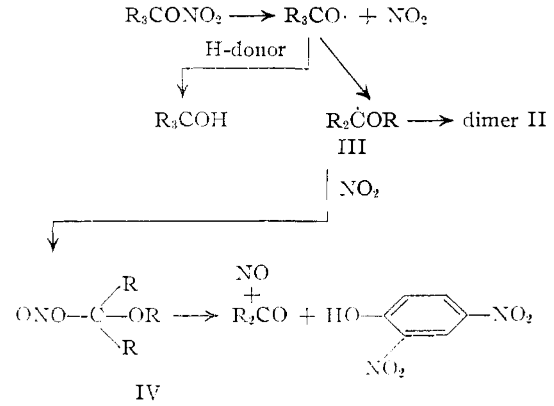


II, R = *p*-nitrophenyl

The fact that the dimer II is obtained in up to 25% yield indicates that the Wieland rearrangement (process 1) occurs to a considerable extent in this particular system and constitutes the first evidence for the occurrence of such rearrangements during the course of the thermal decomposition of a nitrate ester; the high migratory aptitude of the *p*-nitrophenyl group in radical type rearrangements is thus illustrated again.

Although the β-cleavage process 2 proposed by Cristol and Leffler[2] for the thermal decomposition of triphenylmethyl nitrate is certainly applicable to the present case, an alternative path for the production of 4,4'-dinitrobenzophenone and 2,4-dinitrophenol appears attractive in view of the isolation of the benzpinacol (II). This path involves the attack of nitrogen dioxide[10] on the *p*-nitrophenoxy-di-(*p*-nitrophenyl)-methyl radical (III) to produce an unstable nitrite ester IV which in turn may react homolytically with nitrogen dioxide to produce 4,4'-dinitrobenzophenone, 2,4-dinitrophenol and nitric oxide.

The production of equivalent molar quantities of ketone and dinitrophenol predicted by this reaction sequence was experimentally substantiated. The highly colored and unidentified products of the decomposition may also be accounted for by the abstraction of hydrogen atoms from aromatic rings by the tri-(*p*-nitrophenyl)-methoxy radical.



R = *p*-nitrophenyl

Experimental[11]

Preparation of Tri-(*p*-nitrophenyl)-methyl Nitrate (I).—Tri-(*p*-nitrophenyl)-methyl bromide (11.0 g. or 0.024 mole) prepared by the method of Lewis, Lipkin and Magel[12] and melting at 200–201° was brought to reflux in 500 ml. of dry acetonitrile and the mixture cooled to room temperature. To this slurry was added 11.0 g. of silver nitrate dissolved in 50 ml. of dry acetonitrile. The mixture was magnetically stirred in a closed system for two hours at room temperature, filtered and the filtrate concentrated to about 100 ml. under reduced pressure. The crystalline nitrate ester was removed by filtration, washed several times with cooled acetonitrile and dried in vacuum; yield 8.0 g. or 75% of theory. This material melted sharply at 156° with the evolution of nitrogen oxides and fumed on long standing in moist air. The carbon–hydrogen and nitrogen analyses suggest the presence of a small amount of carbinol in the reaction product.

Anal. Calcd. for $C_{19}H_{24}N_4O_9$: C, 51.82; H, 2.74; N, 12.72. Found: C, 52.34; H, 2.57; N, 12.28.

Thermal Decomposition of Tri-(*p*-nitrophenyl)-methyl Nitrate (I).—To 50 ml. of pure, dry chlorobenzene was added 3.83 g. (0.0087 mole) of tri-(*p*-nitrophenyl)-methyl nitrate (I). This solution was heated at 120–130° in a slow stream of oxygen-free nitrogen in such a manner that the exit gases passed through a 10% aqueous solution of ferrous ammonium sulfate. Heating was carried out for seven hours.

During the heating period the ferrous ammonium sulfate became dark brown in color due to the formation of the ferrous ion–nitric oxide complex. This brown color was discharged on heating the solution in air.

The reaction mixture was concentrated to 10 ml. under a small helices-packed column, 50 ml. of methylene chloride was added and the solution extracted three times with dilute sodium hydroxide solution. The organic layer was then washed with water and dried over magnesium sulfate.

Acidification of the aqueous base extract afforded 0.59 g. (0.0032 mole) of nearly pure 2,4-dinitrophenol, m.p. 100–105°, identified by conversion to its bromo derivative, m.p. 117–117.5°. A mixture of the bromo derivative and picric acid melted at 100–110°.

Examination of the crude dinitrophenol by chromatography on paper using aqueous butanol as solvent indicated only one major constituent.

The neutral methylene chloride extract was concentrated to about 15 ml. and placed on a 30-cm. Activity I neutral alumina column and eluted with benzene followed by methylene chloride. Thirty-four 250-ml. fractions were taken. The first fourteen (benzene) gave 1.23 g. (0.0034 mole) of pure 4,4'-dinitrobenzophenone, m.p. 187°, mixed m.p. with authentic sample 187°. The following five fractions (benzene) produced 0.80 g. of material melting at 273–283° and which melted at 289° after several recrystallizations from methylene chloride–petroleum ether. This material gave no hydroxyl or carbonyl bands in the infrared. Refluxing this material with aqueous dioxane or ethylene glycol containing sodium hydroxide produced *p*-nitrophenol (identified by comparison with an authentic sample on a paper

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(10) Although no evidence is available with which to settle the question, the nitrogen dioxide which reacts with rearranged radical in this or similar processes may be "caged" by solvent molecules and have as its ultimate source the nitrate ester molecule from which the alkoxy or rearranged alkoxy radical is derived. See M. Levy, M. Steinberg and M. Szwarc, THIS JOURNAL, **76**, 5978 (1954), for a discussion of a similar case.

(11) All melting points are uncorrected.

(12) C. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

chromatogram). The yield corresponds to 0.001 mole of material.

Anal. Calcd. for $C_{38}H_{24}N_6O_7$: C, 57.87; H, 3.06; N, 10.67. Found: C, 57.45; H, 3.19; N, 10.46.

The material remaining on the column was removed with methylene chloride and proved to be tri-(*p*-nitrophenyl)-carbinol, 0.64 g. (0.0016 mole) melting at 183–186°. This material had an infrared spectrum identical to that of authentic carbinol. A moderate amount of highly colored material remained on the column.

Miscellaneous Reactions of Tri-(*p*-nitrophenyl)-methyl Nitrate (I).—One gram of tri-(*p*-nitrophenyl)-methyl nitrate (I) was dissolved in 50 ml. of dry acetone. One gram of sodium iodide was added and the solution allowed to stand several minutes. The solution was flooded with water and the green tri-(*p*-nitrophenyl)-methyl radical precipitated from the aqueous iodine solution.

The solution of a few crystals of the nitrate ester I in a few drops of concentrated sulfuric acid resulted in the formation of an orange solution identical with that produced by the similar treatment of tri-(*p*-nitrophenyl)-carbinol. The ketone, 4,4′-dinitrobenzophenone gives a nearly colorless solution under the same circumstances.

HUNTSVILLE, ALABAMA

[CONTRIBUTION NO. 680 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Effects of γ-Methyl Substitution on the Rates of the Bimolecular Displacement and Elimination Reactions of Alkyl Halides[1]

BY V. J. SHINER, JR., M. J. BOSKIN AND M. L. SMITH

RECEIVED MARCH 24, 1955

Rate and olefin fraction data are presented which in conjunction with other information available in the literature allow the comparison of elimination rates in each branch as well as substitution rates for the series of compounds $(CH_3)_xCH_{3-x}$–CH_2–CHBr–CH_3 (with *x* equal to 3, 2, 1 and 0 with *ca.* 1 *N* sodium ethoxide in absolute ethyl alcohol). The displacement rate is slowed down progressively by increasing γ-methyl substitution with the extremes differing by a factor of 4.4. The rates of elimination in the left-hand branches vary over-all by a factor of about three and can be correlated with the number of C–H bonds available for hyperconjugation in a manner consistent with the Hughes–Ingold theory.[2] Increasing γ-methyl substitution also slows down the rate of elimination in the right-hand branch. The relation between these data and the problem of the effect of alkyl substitution on hyperconjugation is discussed.

The effects on the displacement and elimination reactions of alkyl halides, of branching alpha and beta to the displaced group have been systematically investigated, correlated and fairly well explained. The work of Brown and Fletcher[3] and of Hughes, Ingold and Shiner[4] shows that extensive branching at the γ-carbon atom also has a surprisingly large effect on the rate of unimolecular reactions of tertiary alkyl halides. For example, 2,4,4-trimethyl-2-chloropentane is solvolyzed around twenty times faster than *t*-butyl chloride to give a high proportion of 2,4,4-trimethylpentene-1 in violation of the Saytzeff rule. However, no studies on the effects of extensive γ-branching on the bimolecular reactions of alkyl halides have been reported. In this paper are reported new rate constants and olefin yields which with previously published data allow the tabulation of elimination rates in each branch as well as substitution rates for the series of compounds $(CH_3)_xCH_{3-x}$–CH_2–CHBr–CH_3 (with *x* equal to 3, 2, 1 and 0) with *ca.* 1 *N* sodium ethoxide in absolute ethyl alcohol. Therefore the step-by-step effect of γ-methyl substitution on the rates of typical bimolecular substitution and elimination reactions can be analyzed. In Table I are tabulated rate constants and olefin fractions for the reactions of 4-methyl-2-bromopentane and 4,4-dimethyl-2-bromopentane with sodium ethoxide in absolute ethanol. Corresponding values for isopropyl bromide are included for comparison.

TABLE I

REACTIONS WITH 1 *N* SODIUM ETHOXIDE IN ABSOLUTE ETHYL ALCOHOL

Compound	Temp., °C.	No. of points	K_2 (10^{-6} l./mole/sec.)	Std. dev.	Olefin fraction
Isopropyl bromide	25.00	12	2.957	0.003	0.640
Isopropyl bromide	35.00	12	10.59	.008	.677
Isopropyl bromide	45.00	12	37.91	.02	.704
Isopropyl bromide	55.00	12	116.2	.6	.731
4-Methyl-2-bromopentane	25.00	12	1.69	.01	.84
4,4-Dimethyl-2-bromopentane	35.00	10	4.72	.03	.87
4,4-Dimethyl-2-bromopentane	45.00	13	15.8	.2	.89
4,4-Dimethyl-2-bromopentane	55.00	14	47.6	.4	.88

Values of the Arrhenius parameters for the reactions of isopropyl bromide and 4,4-dimethyl-2-bromopentane, calculated from the data of Table I by the method of least squares, are tabulated in Table II.

TABLE II

ARRHENIUS PARAMETERS FOR REACTIONS WITH ETHOXIDE IONS IN ABSOLUTE ETHYL ALCOHOL[a]

	E2		SN2	
Compound	Log *A*	E_a	Log *A*	E_a
Isopropyl bromide	12.42	24.8	10.18	22.0
4,4-Dimethyl-2-bromopentane	11.09	23.2	10.23	23.2

[a] Units of *A* are l./mole/sec. Std. deviations in log *A* are 0.01 and in E_a 0.2.

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[1] (a) Abstracted in part from a thesis submitted by M. J. Boskin to the Graduate School of Indiana University in partial fulfillment of the requirements for the M.A. degree. (b) Presented before the Division of Organic Chemistry at the 127th National Meeting of the American Chemical Society, Cincinnati, April 1, 1955. (c) Supported in part by the Petroleum Research fund of the American Chemical Society.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 434 ff.

[3] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[4] E. D. Hughes, C. K. Ingold and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953).