THE THERMAL REVERSIBILITY OF THE MICHAEL REACTION

II. NITROKETONES AND RELATED COMPOUNDS¹

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ABSTRACT

In continuation of the study of the thermal reversibility of Michael adducts, 13 γ -nitroketones were examined in the mass spectrometer, using the inlet heated at 230°. The presence of furans was indicated, arising from the intact molecule. Such remotely related substances would never have been envisaged had not the mass spectrum been available. In contrast to the behavior of delta ketonic nitriles (Part I) only normal retrogression was found. There were many secondary products resulting from extensive decomposition of the expected nitro addend. Not all the products can be isolated by classical procedures, but their presence is predictable, and can be shown by the use of the mass spectrometer. Nine simple nitro- and bromonitro-ethylenes, sensitive to heat alone, were unexpectedly stable in the heated inlet of the mass spectrometer, but did give rise to very small amounts of decomposition products. Phenyl- and 1-naphthyl-nitromethanes, which decomposed completely, gave comparable types of products. Most of these nitro compounds have previously been thermally treated by classical methods.

The γ -nitroketones used in this work are analogous to the δ -ketonic nitriles described in the previous paper (1), and were prepared similarly. In their behavior they differ from the latter in that the expected addend bearing the nitro group was never found, on account of its susceptibility to further degradation.

C ₆ H ₅ CH=CHCOC ₆ H ₄ X-4		C ₆ H ₅ CHCH ₂ COC ₆ H ₄ X-4	4	$C_6H_5CH = CHCOC_6H_4X-4$
$+ C_6H_5CH_2NO_2$	→	C ₆ H ₅ CHNO ₂ I	→	$+ C_6H_5CHO + NO + ?$

In the first chemical investigation 20 years ago (2) three products of the thermal decomposition of I (X = H) were recorded; these were chalcone, benzaldehyde, and nitric oxide. In a renewed chemical investigation, after removal of the benzaldehyde as the 2,4-dinitrophenylhydrazone, benzonitrile, which has a very similar odor, remained; it was identified by infrared and mass spectra. Benzonitrile is present (3.5%) in the more volatile fractions of the thermolysis; however, as the temperature was raised, considerable water appeared along with the nitrile, as though both had resulted from the decomposition of some intermediate product. The latter could be benzaldoxime, a trace of which was found by gas chromatography; it was identified in the mass spectra of several of the fractions. That the nitrile arises from benzaldoxime was confirmed by following the course of the thermal decomposition of the pure oxime at 230° in the heated inlet of the mass spectrometer. The benzaldoxime peaks decreased with time, while those of the benzonitrile were simultaneously increasing. A small amount of benzoic acid was also isolated from the distilled products from I (X = H); this was not surprising, since it could arise by oxidation of the aldehyde by the nitric oxide, or by hydrolysis of the nitrile. When

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the decomposition of this adduct I was examined in the mass spectrometer, by allowing the compound to decompose in the heated inlet, a considerable variety of products were identified (Table I). The ratios of the components changed during the 1-hour observation

TABLE I

Thermal decomposition products identified by mass spectrometer and masses of parent ions, helpful in establishing identifications

Substances	Products
I, X = H, 2 isomers	(296) Triphenylfuran; (208) chalcone; (180) stilbene; (120) aceto-
I, X = C_6H_5	(284) 4'-Phenylchalcone; (30) nitric oxide; many peaks unaccounted
I, X = Cl	tor (330) 2-(4-Chlorophenyl)-4,5-diphenylfuran;† (242) 4'-chlorochal-
I, $X = Br$	(375) 2-(4-Bromophenyl)-4,5-diphenylfuran;† (287) 4'-bromochal-
γ -Br-I; X = Cl	(330) 2-(4-Chlorophenyl)-4,5-diphenylfuran;† (258) bromostilbene;†
γ -Br-I; X = Br	(374) 2-(4-Bromophenyl)-4,5-diphenylfuran;† (286) 4'-bromochal- cone; (262) 1,2-dibromostyrene; (258) bromostilbene;† (30) nitric ovide
II	(220) Diphenylfuran; (132) phenyl vinyl ketone; (small 120) aceto-
111	phenone; (30) nitric oxide
	(208) Chalcolle; (50) Intric Oxide
γ -Br-11	(200) Trinhandfurant, (300) Intric Oxide
γ -Br-1; $X = \Pi$	(290) Tripnenynuran; (208) chaicone
γ -Br-1; $X = CI$	(180) Stillelle (960) 1.9 differences (950) have estilled
γ -Br-1; X = Br	(280) 4 - Bromochalcone; (202) 1,2-dibromostyrene; (259) bromostin-
$C_6H_5CH_2NO_2$	(182) Bibenzyl; (121) benzaldoxime; (119) <i>o</i> -hydroxybenzonitrile; (106) benzaldehyde; (103) benzonitrile; (30) nitric oxide; (78) benzene
$1\text{-}C_{10}H_7CH_2NO_2$	(282) Dinaphthylethane; [†] (169) 2-hydroxy-1-naphthonitrile; [‡] (156) 1-naphthonitrile: (128) naphthalene: (30) nitric oxide
aci-Form	Same, plus (172) 1-naphthoic acid
<i>β</i> -Nitrostvrene	(149) UM:§ (102) phenylacetylene;† (30) nitric oxide
2.5-Dimethoxy-derivative	(209) UM: (30) nitric oxide
2.5-Dimethoxy- <i>B</i> -methyl derivative	(223) UM: (30) nitric oxide
β -Bromo- β -nitrostyrene	(262) 1,2-Dibromostyrene; (258) bromodiphenylethylene;† (228) UM: (30) nitric oxide
1 1-Diphenylethylenes:	
-2-nitro	(225) UM; (30) nitric oxide
4'-phenyl-2-nitro	(301) UM; (30) nitric oxide
2-bromo-2-nitro-	(338) 2,2-Dibromo-1,1-diphenylethylene; (332) tetraphenylethylene;
2,2-dibromo-	(338) UM; (178) tolane

*In all cases when nitric oxide is reported it could not be confirmed because of other possible sources of an NO⁺ ion.

Confirmation is qualified because peaks are very small. §Undecomposed molecule.

period, while the cracking patterns of the components remained constant in all of the spectra. All of the identifications tabulated were confirmed by comparison with reference spectra, of known compounds unless otherwise noted. Adduct I gave 2,3,5-triphenyl-furan, stilbene, chalcone, and nitric oxide; which presumably arise from the intact adduct. The furan and chalcone were estimated by gas chromatography. Many of the smaller molecules may be attributed to the very heat-sensitive phenylnitromethane, formed by retrogression. In this and in all other instances where nitric oxide is reported, its presence could not be confirmed by a reference mass spectrum because of the alternate possible source of an NO⁺ ion fragment from most nitro compounds. However, nitric oxide was identified chemically as a product of the independent laboratory decomposition reaction

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of I. There was no definite indication of an abnormal dissociation, which would yield α -nitrostilbene and acetophenone. Both diastereomeric adducts behaved in a similar manner. γ -Bromo derivatives of I gave 3-bromo-2,4,5-triphenylfurans (2). At the time of the classical type of investigation the furan found was not even envisaged because of its seemingly remote relation to the bromonitro ketone; *it could have been predicted had a mass spectrometer been available*! The less highly arylated diphenyl- γ -nitroketone (II) (3) decomposed in the mass spectrometer inlet to yield diphenylfuran, vinyl phenyl ketone, nitric oxide, and a little acetophenone. Its isomer (III) gave chalcone and nitric oxide; none of the expected nitromethane was found, it being unstable under the experimental conditions.

CH ₂ CH ₂ COC ₆ H ₅	C ₆ H ₅ CHCH ₂ COC ₆ H ₅
C ₆ H ₅ CHNO ₂	H_2NO_2
II	III

The γ -bromo derivative of II gave 2,5-diphenylfuran and nitric oxide. This is at variance with the chemical finding (3) that heat alone gives rise to 3-bromo-2,5-diphenylfuran. Two γ -bromo derivatives corresponding to I gave complex mixtures, among which the previously detected chalcones and nitric oxide predominated, but in each instance there was some triarylfuran.

With a view to further elucidating these results, phenylnitromethane itself was examined in the mass spectrometer. It decomposed in the heated inlet, yielding a mass spectrum consistent with a mixture containing bibenzyl (1,2-diphenyl ethane), benzaldoxime, benzaldehyde, benzonitrile, benzene, nitric oxide, and an unknown giving a very small peak at mass 119, but no stilbene. Benzaldehyde, dibenzhydroxamic acid, nitric oxide, and water have been previously reported as products of thermolysis (4). Since phenylnitromethane is an unstable liquid that is not easily purified, α -naphthylnitromethane, which can be crystallized to constant melting point, was next examined. After exposure in the mass spectrometer at 230°, the analytically pure compound gave a spectral pattern corresponding to a mixture of dinaphthylethane, α -naphthaldehyde, α -naphthonitrile, naphthalene, nitric oxide, and an unknown giving a very small peak at mass 169. The aci-form, which is an oil, gave all the same products, plus a little α -naphthoic acid; however, there appeared to be more of the unknown and naphthonitrile. There was no α -naphthaldoxime, but a separate examination of this substance in the mass spectrometer at 230° revealed such a rapid decomposition to the unknown (169) and nitrile that its absence was not surprising. These results are analogous to and correspond with those found with the phenylnitromethane. Since there was no dinaphthylstilbene, it may indicate that the stilbene found on heating the adduct I probably arises from the latter structure rather than from the phenylnitromethane.

In view of these complex results, all the nine nitro- and bromo-nitroethylenes, available from the previous work (3), were examined in the mass spectrometer. Rather surprisingly, they were all relatively stable under the prevailing conditions, each giving a peak corresponding to the molecular weight of the original undecomposed molecule, with very little nitric oxide; there were peaks that could be attributed to the respective phenylacetylenes, although these were not confirmed. The changing ratio of these peaks with respect to the parent peak of the undecomposed molecule was accepted as proof that these peaks represented reaction products. This is in agreement with the chemical evidence; β -nitrostyrene can be distilled with some decomposition (b.p. 250–260°) (5). β -Bromo- β -nitro- α , α -diphenylethylene also showed a peak at its molecular weight, but partially decomposed to

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give some β,β -dibromo- α,α -diphenylethylene and tetraphenylethylene. β -Bromo- β -nitrostyrene showed the parent undecomposed molecule, plus 1,2-dibromostyrene and a monobromödiphenylethylene. β,β -Dibromo- α,α -diphenylethylene showed the parent molecule and tolane (diphenylacetylene). The latter and 1,2-dibromostyrene have been shown previously (2) by chemical methods.

DISCUSSION OF RESULTS

The formation of 2,3,5-triphenylfuran, which contains *all* the carbon atoms of the chalcone-phenylnitromethane adduct I indicates that it is not a retrogression product. In this instance, the yield of furan is low, whereas with the bromonitro ketones, the yield of bromofuran was very high; the difference is one of degree rather than kind. The adduct, either as such or in its *aci*-form, has lost nitrous acid, possibly to give the carbene (IV),² from which a hydride ion is removed under the prevailing oxidizing conditions. An alternate possibility, the direct displacement of nitrite ion by the free electron pair of the oxygen atom, seems less likely since the analogous cyano adduct (1) does not show a similar behavior, no furan being formed.³



In the retrogression to chalcone and arylnitromethane, the behavior of the arylnitromethane can be summarized as shown in Chart I.



Chart I. Possible paths of decomposition of arylnitromethanes.

The unknown giving a peak of mass 119 could be benzonitrile oxide (6), benz[4,5]isoxazole (indoxazene), or its conversion product o-hydroxybenzonitrile (salicylonitrile) (7), all of molecular weight 119. The first two were excluded by comparison with mass spectra of authentic specimens. The unknown giving a peak at mass 169 could be a benzolog of any of the three; it is probably 2-hydroxy-1-naphthonitrile (8). Owing to the small size of the mass peaks, the identification of the hydroxynitriles (possible parent peaks at m/e119 and 169) is inconclusive; products corresponding to these molecular weights could not be isolated in the laboratory. The hydroxynitriles are probably formed as a result of the

²The intermediate formation of a carbene, as proposed in an earlier paper (2), seems to have been overlooked by subsequent workers in the carbene field.

⁸The referee suggested an alternative mechanism, involving the beta-elimination of nitrous acid, and nucleophilic addition, followed by oxidation to the furan.



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known easy cleavage (7) of an indoxazene; the latter undoubtedly arises by formation of an additional ring which results from a dehydrogenation under the prevailing oxidizing conditions.

EXPERIMENTAL

The substances used for the thermolyses and the reference compounds were on hand from previous work⁴ or were prepared by methods given in the literature, e.g., phenylnitromethane (9), 1-naphthylnitromethane (10), o-hydroxybenzonitrile (7), and 2-hydroxy-1-naphthonitrile (8).

Both stereomeric forms of the adduct (I) gave the same products, when heated for 0.5 hour in vacuo at 214-286°. Water appeared at 238°, and much unchanged adduct distilled; even at atmospheric pressure a little adduct comes over. This indicates that the nitroketones are more stable thermally that the cyanoketones (delta ketonic nitriles (1)). The evolved gas is nitric oxide (colorless, turns brown in air). The distillate from 5 g of adduct was collected in fractions for examination by gas chromatography; the percentages of the components given are totals. The main products were benzaldehyde (52%) and chalcone (35%). Lesser products were 2,3,5-triphenylfuran (19%), benzonitrile (3.5%), benzaldoxime (a trace), and benzoic acid. The benzaldehyde, benzaldoxime, and benzonitrile were chromatographed as before (1), the retention times being 3.87, 9.02, and 4.18 minutes, respectively. The chalcone and triphenylfuran were chromatographed in a Barber-Colman Model 10 Gas Chromatograph, containing the Lovelock ionization detector, with radium sulphate as the ionizing source. The conditions of the separation were as follows: the column contained 5%, by weight, of General Electric SE-30 silicone gum rubber on 80-100 mesh, acidwashed Celite 545. The column was 5 ft long, and was operated at 200° C with a flow rate of approximately 50 ml/minute. The retention times of chalcone and triphenylfuran were 0.48, 2.23 minutes, respectively.

Mass spectrometry.—The mass spectrometer used was described previously (1). The peaks found in the mass spectra and their identification by comparison of the entire pattern, with known reference compounds, are summarized in Table I.

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