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THE ACTION OF HEAT ON CERTAIN BROMONITRO COMPOUNDS

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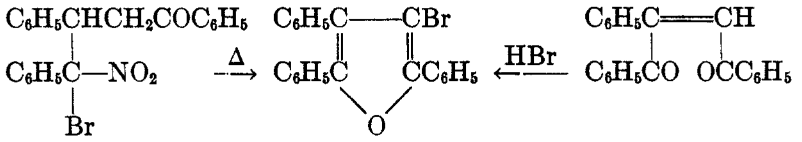
When either stereoisomeric form of γ-bromo-γ-nitro-β,γ-diphenylbutyrophenone (I) was heated slightly above the melting point, gas was evolved; the late Professor Kohler suggested to the senior author that a study of its decomposition would be of interest. In this paper are described the results secured when these and other bromonitro compounds are pyrolyzed.

Both forms of the nitro ketone (I) gave off a brown gas and yielded the same chemically inactive, white substance, $C_{22}H_{15}BrO$, formed by a loss of nitrogen dioxide and water. From the empirical formula and nonreactivity, it was assigned the structure, 2,3,5-triphenyl-4-bromofuran, (II) and the correctness of this was shown by

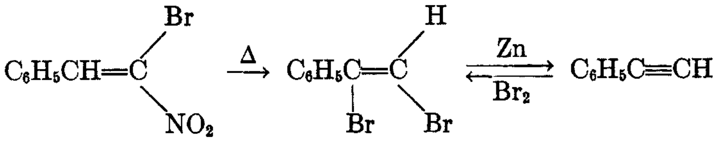


I II

a synthesis from α,β-dibenzoylstyrene and hydrogen bromide (1). In a similar manner homologs were secured from other corresponding bromonitro ketones.

γ-Nitro-β,γ-diphenylbutyrophenone (I, H for Br) also decomposes on heating, with evolution of oxides of nitrogen. The other products are benzaldehyde and benzalacetophenone. This decomposition is of an entirely different nature from that of the bromonitro ketone; the products are what one would expect if the nitro ketone dissociated into its components, phenylnitromethane and the unsaturated ketone, the former being the source of the aldehyde and oxides of nitrogen.

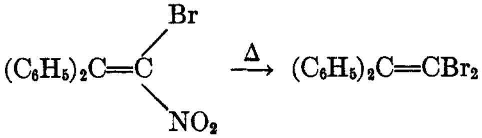
β-Bromo-β-nitrostyrene (III) was next submitted to pyrolysis. It, too, evolved nitrogen dioxide when heated above its melting point. In this case the reaction was not as clean, considerable carbonaceous matter being formed, but the principal product was α,β-dibromostyrene, IV; there was also a small amount of benzoic acid. The structure of the dibromide (2) (IV) was shown by repeating Nef's procedure, namely, debromination with zinc dust to yield phenylacetylene and synthesis from the latter and bromine.



$$C_6H_5CH{=}C(Br)(NO_2) \xrightarrow{\Delta} C_6H_5C(Br){=}C(H)(Br) \underset{Br_2}{\overset{Zn}{\rightleftarrows}} C_6H_5C{\equiv}CH$$

III IV

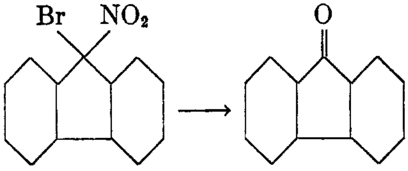
When β-bromo-β-nitro-α,α-diphenylethylene (V) was pyrolyzed, it gave β,β-dibromo-α,α-diphenylethylene (VI) as shown below. The latter was identified by comparison with a specimen secured by a known procedure (3).



$$(C_6H_5)_2C{=}C(Br)(NO_2) \xrightarrow{\Delta} (C_6H_5)_2C{=}CBr_2$$

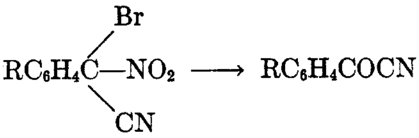
V VI

A search of the literature revealed a few additional instances of the decomposition by heat of bromonitro compounds in which the bromine atom and the nitro group are on the same carbon atom. 9-Bromo-9-nitrofluorene (VII) yields fluorenone (4); several aryl bromonitrocyanomethanes yield

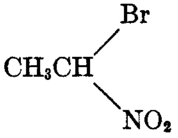


VII

aroyl cyanides (5);



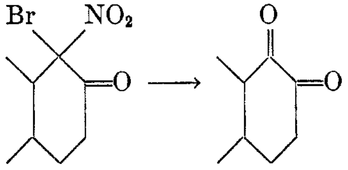
$$RC_6H_4C(Br)(NO_2)(CN) \longrightarrow RC_6H_4COCN$$



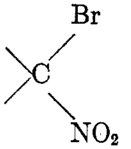
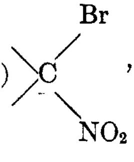
$$CH_3CH(Br)(NO_2)$$

VIII

bromonitromalonic ester gives oxomalonic ester (6); polynuclear *o*-bromo-*o*-nitro ketones give *o*-quinones (7);



and a nitrobromo ketone (a) in the benzene series gives a toluquinone (8), (b) in the camphor series gives camphorquinone (9), and (c) in the pyrazolone series gives a pyrazoldione (10).

A considerable number of liquid halonitro compounds of the aliphatic series has been described, many of which decompose on distillation or cannot be distilled. The nature of the decomposition products has seldom been determined and no distinction has been made between bromine and nitrogen dioxide, both possible and both reddish-brown gases. A careful study of chloropicrin has shown that it slowly decomposes at its boiling point, and that the products are phosgene and nitrosyl chloride, $CCl_3NO_2 \rightarrow COCl_2 + NOCl$.[1] Even with bromonitroethane (VIII), which is recorded in the literature as distilling without decomposition, it has been found that during the distillation enough gas is evolved to color iodo-starch paper deeply, indicating the presence of nitrogen dioxide and/or bromine. It will be seen that in practically all the instances in which the nature of the products has been determined, the net result of the decomposition has been to replace  $\rangle C\langle^{Br}_{NO_2}$ by $\rangle C{=}O$ and that the formation of a ketone "appears to be characteristic for secondarily bound groups (4)  $\rangle C\langle^{Br}_{NO_2}$". That this conclusion cannot be wholly correct is evident from the variety of examples described in this paper.

The formation of the bromofuran (II) from the bromonitroketone (I) would, at first sight, seem to be of an entirely different nature. One would

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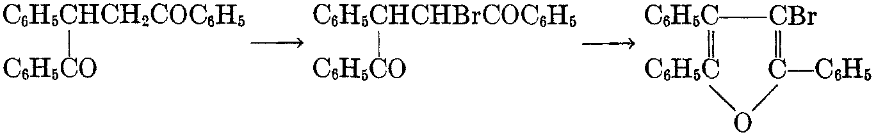
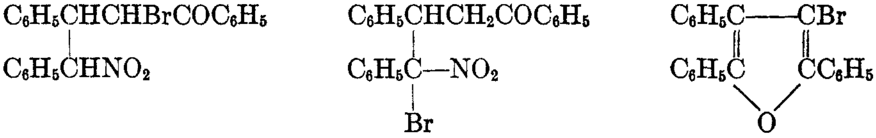
[1] Gardner and Fox, *J. Chem. Soc.*, **115**, 1189 (1919). The nitrosyl chloride was not identified, but the gases evolved passed through concentrated sulfuric acid to absorb nitric oxide. "Hydrogen chloride was either allowed to escape or in some experiments collected in copper sulfate solution."

expect to find desylacetophenone (IX). However, it has been shown (11) that when desylacetophenone is brominated, the only product is triphenylbromofuran (II), except under special experimental conditions. Thus, the production of the bromofuran would be expected if the intermediate step of the pyrolysis were the ketone IX, and it may be safely assumed that the reaction proceeds in this manner. On comparison of the formulas



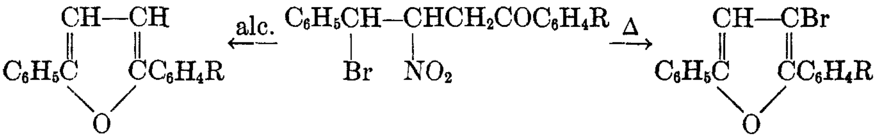
IX II

I and II, it will be noted that in the bromofuran the bromine atom appears in combination with the carbon atom that was alpha to the carbonyl group in the bromonitro ketone. This might seem to indicate that the bromine was always there and never in the gamma position. Other evidence excludes this possibility. The bromonitro ketone was secured by bromination of the nitro ketone in the form of its sodium derivative; it has been shown by Hantzsch (12) that in aliphatic nitro compounds only the hydrogen atom in the alpha position to the nitro group is replaced by bromine when the salt of the *aci*-nitro compound is so treated. Further, the four possible stereoisomeric α-bromo-γ-nitro ketones (XII) are all known and different in melting points and reactions (13).



XII I II

A few other instances of the formation of 4-bromofurans by heating bromonitro ketones (X) are known; these ketones are of a different type, however. In boiling alcoholic solution they give the unbrominated furans

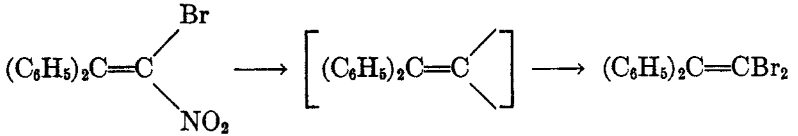


X

(14), which may indicate that ring closure precedes bromination during the pyrolysis. However, this reaction is not strictly parallel to the one under discussion. The formation of 2,5-diphenyl-3-bromo- and -3,4-dibromo-furans by heating an acetic acid solution of γ-bromo-γ-nitro-γ-phenylbutyrophenone is readily accounted for by the mechanism proposed for the triphenylbromofuran II.

The ethylenic bromonitro compounds, III and V, fall into a different category. If the pyrolysis took the same course, ketenes or their reaction products (e.g., diphenylacetic acid) should result. There is no evidence that such is the case, since none of the anticipated substances was found. Their non-isolation, however, is inconclusive, as the decompositions were not quantitative, and there was in these instances a considerable amount of tar.

The assumption of the transitory existence of a bivalent free radical during the pyrolysis enables one to account for the products in a more satisfactory manner. Thus, the diphenylbromonitroethylene (V) would yield radical XI; the latter might combine with either the bromine or oxygen present. Addition of the former would yield the dibromide (VI) actually found, whereas oxygen should give diphenylketene. If this

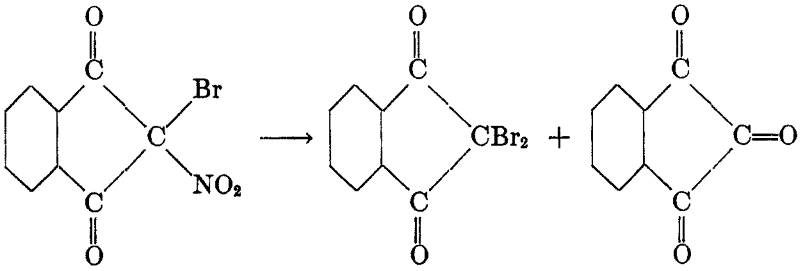


$$(C_6H_5)_2C{=}C(Br)(NO_2) \longrightarrow \left[(C_6H_5)_2C{=}C\langle\right] \longrightarrow (C_6H_5)_2C{=}CBr_2$$

V XI VI

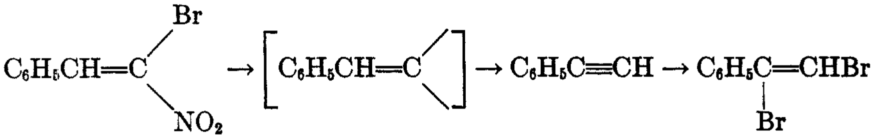
mechanism were applied to 9-bromo-9-nitrofluorene, one might expect to isolate the known 9,9-dibromofluorene, whereas fluorenone is actually obtained. Further, 9-nitrofluorene pyrolyzes to fluorenone (4) which may indicate that oxidation rather than bromination occurs with the saturated bromonitro compounds.

2-Bromo-2-nitroindandion-1,2 (XIX) and the 2-chloro analog decompose when heated; in this instance not only is the expected ketone ninhydrin (XX) formed (15), but also a larger amount of 2,2-dibromoindandion-1,3 (XXI), the combined yields accounting for nearly all of the starting material. These results would lead one to prefer the mechanism involved in the intermediate formation of a bivalent radical, which then combines with either bromine or oxygen, or both, as in this example.



XIX XXI XX

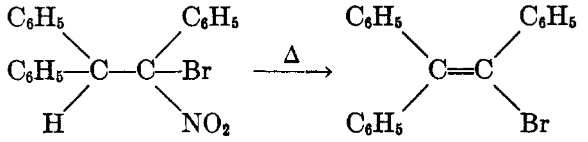
In the case of the bromonitrostyrene (III), the intermediate radical would undoubtedly be even less stable, since it has a hydrogen atom that could rearrange to yield a more stable form, phenylacetylene. The addition of bromine to this would furnish the dibromostyrene actually found and also independently synthesized by this very reaction.



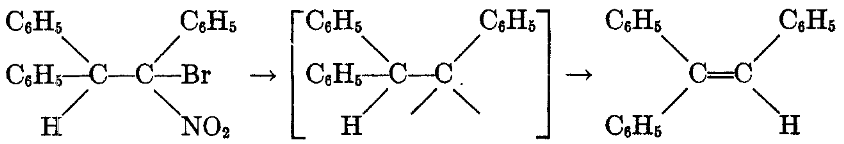
III IV

β,β-Dibromo-α,α-diphenylethylene (VI) is unchanged at the temperature of the pyrolysis; this may indicate that the bromine adds to the bivalent radical (XI) before it has time to rearrange, i.e., that a phenyl group migrates less readily than a hydrogen atom. When this dibromo derivative is heated in boiling benzene with metallic sodium, it loses the bromine and tolane results (26), showing that the radical is capable of rearrangement. Tolane has also been secured from the monobromodiphenylethylene by the action of sodium hydroxide at high temperature (16). Since the monobromide undergoes a Wurtz synthesis, a reaction that is known to proceed *via* radicals, it is evident that a fragment of this type is capable of transitory existence; hence, there is sufficient basis for the assumptions above as to the nature of the intermediates in the pyrolysis reaction.

When 1,1,2-triphenyl-2-bromo-2-nitroethane (XIII) is heated, the product is bromotriphenylethylene (XIV) (17). This behavior is different from that of all the other bromonitro compounds. The authors explain it as a simple loss of HNO_2. However, it can be accounted for by the bivalent radical mechanism following a sequence of reactions similar to that for bromonitrostyrene. The radical XV has an available hydrogen



XIII XIV



XIII XV XVI

for rearrangement and the rearranged product, XVI, might be easily brominated to XIV.

If bivalent radicals of this nature were intermediary in the case of the bromonitro ketones, the products anticipated would be of an entirely different nature from those actually found. Hence, this mechanism, if correct, is only of limited application.

In view of the many above instances, it would seem that "the transformation of phenylbromocyanonitromethane into its metabromo isomeride" is not a "case of intramolecular meta migration" (27) but a bromination, the bromine coming from the decomposition of a second molecule.

EXPERIMENTAL

A. Bromonitro ketone series.—The general procedure for securing the γ-nitro ketones was as follows: a mixture of 2 g. of phenylnitromethane, an equivalent quantity of unsaturated ketone, and 17 cc. of methanol was made alkaline with concentrated sodium methoxide; an immediate white precipitate formed—this usually gradually dissolved with refluxing. After an hour, or sooner, if the flask contents solidified, the whole was acidified with 3 cc. of acetic acid in 17 cc. of methanol. After boiling for 5 minutes and cooling, the addition products were triturated and filtered. When the stereoisomers were separated, the high-melting form crystallized first, in yields of 60–80%; the yield of the low-melting form, which was slowly deposited from the filtrate, was 5–15%. γ-Nitro-β,γ-diphenylbutyrophenone (13), the *p*-methoxy (18) and one stereoisomeric form of the *p*-bromo (19) homologs have already been described. The properties of the other addition products are collected in Table I.

TABLE I

PROPERTIES OF ADDITION PRODUCTS

NO.	NITRO KETONE γ-NITRO-β, γ-DIPHENYL-	M.P., °C.	FORMULA	CALC'D %		FOUND %	
				Br	N	Br	N
XXIII	-4-Chloro-butyrophenone	171	$C_{22}H_{18}ClNO_3$		3.7		3.6
XXIV	-4-Chloro-butyrophenone	116	"		3.7		3.7
XXV	-2-Methyl-5-i-propylbutyrophenone	147	$C_{26}H_{27}NO_3$		3.5		3.4
XXVI	-4-Phenylbutyrophenone	180	$C_{28}H_{23}NO_3$		3.3		3.3
XXVII	-4-Bromobutyrophenone	180	$C_{22}H_{18}BrNO_3$	18.9		18.6	
XXVIII	-4-Bromobutyrophenone	125	"	18.9		18.7	

Since benzal-4-phenylacetophenone was insoluble in hot methanol, the reaction was carried out in 25 cc. of dioxane, and the solvent evaporated on the steam-bath.

The bromonitro ketones (I) were prepared by suspending 3 g. of the addition product in 40 cc. of hot methanol, adding slightly over one equivalent of concentrated sodium methoxide, and stirring until dissolved; an excess of methoxide was avoided. The solution was then chilled in ice-water and bromine was added until a permanent color resulted; after standing for some time sodium bromide separated. Water

(15 cc.) was added, the whole shaken vigorously, and the excess bromine removed by a little sodium bisulfite. The crude bromination product was filtered and washed with methanol; the yield was practically quantitative. Recrystallization was from chloroform-methanol. In most instances the mixture of stereoisomers was used for pyrolysis. Two have been described previously (13, 18). γ-Nitro-γ-bromo-β, γ-diphenylbutyro-(4-chloro)-phenone, m.p. 126° (XXIX), γ-nitro-γ-bromo-β,γ-diphenylbutyro-(4-bromo)-phenone, m.p. 157° (XXX), and γ-nitro-γ-bromo-β,γ-diphenylbutyro-(2-methyl-5-i-propyl)-phenone, m.p. 138° (XXXV) are new.

Anal. Calc'd for $C_{22}H_{17}BrClNO_3$ (XXIX): N, 3.1; for $C_{22}H_{17}Br_2NO_3$ (XXX): Br, 31.8; for $C_{26}H_{26}BrNO_3$ (XXXV): N, 2.9.

Found: (XXIX) N, 2.8; (XXX) Br, 31.5, 31.6; (XXXV) N, 2.7.

Pyrolysis.—The bromonitro ketone (20 g.) was heated in a wide-mouthed flask at 180–200° as long as gases were evolved (15–20 minutes). If pyrolysis was in a closed system, the brown gas at first given off soon became colorless, but was reoxidized to nitrogen dioxide when air was blown through. A few water-drops collected and an odor similar to benzonitrile was noted. The cooled melt was dissolved in chloroform and filtered into 3 volumes of methanol; the bromofuran soon separated in rosettes of needles. The yields were 60–70%, being much lower when air was excluded during the pyrolysis. In one instance a trace of benzoic acid was isolated. Three of the bromofurans have been described previously (1); the properties of the others are collected in Table II. Whenever possible the identity was assured by comparison with the original specimens and mixed melting points (4-chloro, 4-bromo, 4-methoxy). Both stereoisomeric forms of the bromonitro ketones gave the same furan in the same yield. 2,3-Diphenyl-5-(4′-xenyl)-4-bromofuran (XXXI) was also synthesized from the corresponding dibenzoylstyrene (1).

TABLE II

NO.	GROUP IN POSITION 5	M.P., °C.	FORMULA	ANALYSES					
				Calc'd %			Found* %		
				C	H	Br	C	H	Br
II	Phenyl	129	$C_{22}H_{15}BrO$	70.4	4.0	21.4	70.1	4.0	22.0
XXXI	4-Xenyl	193	$C_{28}H_{19}BrO$			17.7			17.4
XXXII	4-Bromophenyl	157	$C_{22}H_{14}Br_2O$			35.2			35.1, 35.3

* These substances were very difficult to burn, or destroy by fuming nitric acid.

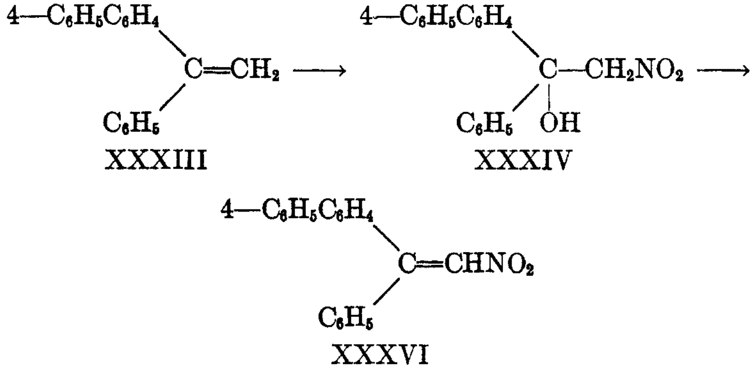
B. Bromonitrostyrene series.—The pyrolysis of β-bromo-β-nitrostyrene (20) was carried out in the same manner, at 190–200°; when gas was no longer evolved, the liquid was distilled, leaving a considerable carbonaceous residue. The distillate (3 g. from 5 g. of the styrene) had an odor resembling benzonitrile, and contained small amounts of benzoic acid. On redistillation the greater portion was found to be α,β-dibromostyrene, b.p. 253–4°.

Anal. Calc'd for $C_8H_6Br_2$: C, 36.6; H, 2.3. Found: C, 36.2; H, 2.4.

When 75 g. of the bromonitrostyrene was submitted to pyrolysis, 29 g. of crude dibromostyrene and 1.3 g. of benzoic acid were obtained; 2.5 g. of the starting material was recovered. It was not possible to isolate or identify benzonitrile from any fraction of the distillate.

The bromine was removed from the dibromostyrene by zinc, following Nef's procedure (2), and the phenylacetylene converted into the characteristic bright yellow copper derivative. A portion of the dibromostyrene was oxidized to benzoic acid by potassium permanganate, showing that no bromine had entered the nucleus.

C. Diphenylethylene series.—The necessary β-nitro-α,α-diphenylethylene was secured by Lipp's procedure (21); though the yields were erratic (48–57%), the method proved to be consistently better than the apparently simpler methods (22). β-Nitro-α-phenyl-α-(4-xenyl)ethylene (XXXVI) was obtained as follows:



XXXIII XXXIV XXXVI

Six grams of the hydrocarbon XXXIII (23) in 35 cc. of carbon tetrachloride was chilled to −10–0°, and the gases, generated by dropping concentrated sulfuric acid upon solid sodium nitrite and dried by phosphorus pentoxide, were passed through for 4 hours. The temperature was not allowed to rise above 0°. The solution was then washed with 25 cc. of water, dried with calcium chloride, and the solvent allowed to evaporate spontaneously. The resulting semi-solid mass was triturated with ether-petroleum ether, and filtered. The carbinol XXXIV separated from ether, on dilution with petroleum ether, in fine white needles, m.p. 136°.

Anal. Calc'd for $C_{20}H_{17}NO_3$: N, 4.4. Found: N, 4.3.

The solvent was evaporated from the residual solution from the isolation of the above carbinol, and the gum taken up in 25 cc. of acetyl chloride. After refluxing for an hour, the mixture was decomposed by iced sodium carbonate, the sticky, insoluble product taken up in ether and dried by potassium carbonate. Petroleum ether was then added to incipient cloudiness; on chilling, yellow crystals of the nitroethylene (XXXVI) separated. They crystallized from petroleum ether or methanol in fine prisms, m.p. 134°. The filtrate deposited a mixture of both possible geometrical isomers, which was separated mechanically; the low-melting form crystallized in needles, m.p. 114°.

Anal. Calc'd for $C_{20}H_{15}NO_2$: C, 79.7; H, 5.0; N, 4.7.

Found: (134°) C, 79.6; H, 5.1; N, 4.4; (114°) C, 79.8; H, 5.3; N, 4.7.

That the nitro group was not on one of the aromatic nuclei was shown by oxidation of the unsaturated nitro compound to the known phenyl-4-xenyl ketone, by refluxing an acetone solution with excess potassium permanganate for 15 minutes, destroying unused oxidizing agent by alcohol, filtering, evaporating, and recrystallizing the ketone from methanol; the melting point was 101°, and was not depressed on admixture with an authentic specimen (24).

β-Bromo-β-nitro-α,α-diphenylethylene (V).—Three lots, of 5.1 g. each of β-nitro-α,α-diphenylethylene (XXII) were dissolved separately in 10 cc. of chloroform, and 5 g. of bromine in 10 cc. of the same solvent added. There was no immediate action, but after several hours hydrogen bromide was slowly given off. After 24 hours, the solutions were combined, unused bromine was removed by sodium bisulfite solution, and the solvent was evaporated from the washed and dried (sodium sulfate) solution. The residue was taken up in methanol, and, on addition of water to incipient crystallization, 14 g. of yellow prisms separated. Purification from methanol gave 9 g. (43%) of pure compound, m.p. 91°.

Anal. Calc'd for $C_{14}H_{10}BrNO_2$: N, 26.3; Br, 4.6. Found: N, 26.0; Br, 4.7.

Pyrolysis.—The procedure was, in general, the same as with the other bromonitro compounds. Gas bubbles first appeared at 145–150°, and the highest temperature of the bath was 300°; 8 g. of substance lost 1 g. in weight. The residue was removed by ether and methanol, and steam-distilled; only 0.2 g. of product was carried over while 2 liters of water was being collected. The residual mixture was extracted with ether, and this solvent replaced by methanol; the latter was treated with Darco and the filtrate diluted by 1 cc. of water. On standing for some time, 1.5 g. of the dibromoethylene (VI) was obtained as fine, white needles, m.p. 83.5°.

Anal. Calc'd for $C_{14}H_{10}Br_2$: Br, 47.3. Found: Br, 47.3, 47.4.

It was compared with an authentic sample secured by the directions of Goldschmiedt (3); the melting points and mixed melting points were 83.5°.

Pyrolysis of γ-Nitro-β,γ-diphenylbutyrophenone.—The nitro ketone (3.5 g.) was heated in an oil bath in the same manner as described under the bromonitro compounds; oxides of nitrogen, and steam, were given off. After one hour, the cooled melt was taken up in alcohol-chloroform, and treated with Darco and Norit. The oil that remained after evaporation of the solvent smelled strongly of benzaldehyde; since it failed to crystallize, the aldehyde was removed by steam distillation. The oily residue was removed, a portion dissolved in methanol and converted into the 2,4-dinitrophenylhydrazone of benzalacetophenone (25), m.p. 245°.

α-Bromo-α-nitroethane.—There is no mention in the literature of any decomposition of this substance during distillation. However, when 8 g. was distilled in the ordinary manner, using a water condenser, starch-iodide paper was turned deep blue, even at the outlet of the receiving flask, throughout the distillation. This indicated that decomposition was occurring.

SUMMARY

1. Pyrolysis of γ-bromo-γ-nitro ketones yields bromofurans.
2. With ethylenic bromonitro compounds, the products are α,β- or β,β-dibromostyrenes.
3. Mechanisms have been proposed to account for both reactions.

Rochester, N. Y.

REFERENCES

(1) Allen and Rosener, *J. Am. Chem. Soc.*, **49**, 2110 (1927).
Allen and Hubbard, *ibid.*, **52**, 384 (1930).
(2) Kinnicutt and Palmer, *Am. Chem. J.*, **5**, 385 (1884).
Nef, *Ann.*, **308**, 273 (1899).
(3) Goldschmiedt, *Ber.*, **6**, 985 (1873).
(4) Wislicenus, W., and Waldmüller, *Ber.*, **41**, 3340 (1908).
(5) Wislicenus, W., and Elvert, *Ber.*, **41**, 4132 (1908).
Wislicenus, W., and Schäfer, *ibid.*, **41**, 4169 (1908).
Wislicenus, W., and Fischer, M., *ibid.*, **43**, 2239 (1910).
Flürscheim and Holmes, *J. Chem. Soc.*, **1928**, 478, 479.

(6) Willstätter and Hottenroth, *Ber.*, **37,** 1781 (1904).
(7) Fries, *Ann.*, **389,** 315 (1912).
Fries and Roth, *ibid.*, **389,** 319 (1912).
Armstrong and Rossiter, *Proc. Chem. Soc.*, **1887,** 144; **1891,** 87.
(8) Auwers and Burrows, *Ber.*, **32,** 3043 (1899).
(9) Lapworth, *J. Chem. Soc.*, **59,** 322 (1896).
(10) W. Wislicenus and Göz, *Ber.*, **44,** 3491 (1911).
(11) Allen and Herrmann, *J. Am. Chem. Soc.*, **51,** 3591 (1929).
(12) Hantzsch, *Ber.*, **29,** 699, 2251 (1896).
(13) Kohler, *J. Am. Chem. Soc.*, **46,** 1733 (1924).
(14) Kohler and Engelbrecht, *J. Am. Chem. Soc.*, **41,** 1382 (1919).
Kohler and Williams, *ibid.*, **41,** 1650 (1919).
Kohler and Smith, *ibid.*, **44,** 629 (1922).
Allen and Bridgess, *ibid.*, **51,** 2155 (1929).
(15) Wanag and Loder, *Ber.*, **71,** 1267 (1938).
(16) Lipp, *Ber.*, **56,** 570 (1923).
(17) Kohler and Stone, *J. Am. Chem. Soc.*, **52,** 761 (1930).
(18) Kohler and P. Allen, *J. Am. Chem. Soc.*, **50,** 889 (1928).
(19) Kinney, C. R., *Dissertation*, pp. 55-6. Harvard University. **1925.**
(20) Thiele, *Ann.*, **325,** 8 (1902).
Steinkopf, *J. prakt. Chem.*, **84,** 712 (1911).
(21) Lipp, *Ann.*, **449,** 21 (1926).
(22) Wieland and Rahn, *Ber.*, **54,** 1773 (1921).
Anschütz and Hilbert, *ibid.*, **54,** 1857 (1921).
(23) Schlenk and Bergmann, *Ann.*, **464,** 32 (1928).
(24) Staudinger and Kon, *Ann.*, **384,** 97 (1911).
(25) Allen and Richmond, *J. Org. Chem.*, **2,** 225 (1937).
(26) Harris and Frankforter, *J. Am. Chem. Soc.*, **48,** 3144 (1926).
(27) Flürscheim and Holmes, *J. Chem. Soc.*, **1928,** 469.