0.00507 mole per liter. According to the data of Hildebrand,[10] the value of S should be between 13.1 and 13.9 for a normal liquid. The values obtained for S were 14.7 for mononitrothiophene and 14.8 for dinitrothiophene, thus indicating that neither is a normal liquid within the range of temperature considered.

Acknowledgment

The authors desire to express their sincere acknowledgment to Professor Warren W. Ewing for numerous helpful suggestions and assistance during the progress of this study.

Summary

A study of the literature showed a marked absence of critical data for the thiophene series.

The vapor pressures of mononitro- and dinitrothiophene were measured, and their theoretical boiling points, molar latent heats of vaporization and entropies of vaporization calculated.

Mononitrothiophene showed no decomposition at the maximum temperature to which it was subjected. Dinitrothiophene was found to decompose above 250° and to attack mercury at much lower temperatures.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

ADDITION REACTIONS OF VINYL PHENYL KETONE. I. PHENYLNITROMETHANE

BY CHARLES F. H. ALLEN AND M. PHILBRICK BRIDGESS

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Vinyl phenyl ketone (I) is the lowest member of the series of unsaturated phenyl ketones having a conjugated system. It should be of interest to compare the properties and reactions of the products derived from it by the addition of certain substances having active hydrogen with those obtained by the addition of the same compounds to a substituted vinyl phenyl ketone, such as benzalacetophenone (II)

$$\underset{\text{I}}{CH_2{=}CHCOC_6H_5} \qquad \underset{\text{II}}{C_6H_5CH{=}CHCOC_6H_5} \qquad \underset{\text{III}}{CH_2ClCH_2COC_6H_5}$$

Since it combines very readily with substances[1] that have an active hydrogen atom, it can be used for making saturated ketonic compounds which are unsubstituted in the beta position and which it is difficult to secure in any other manner. It seemed probable that these addition products could be converted into other substances which would be useful in connection with the study of reactions of which the mechanism is at

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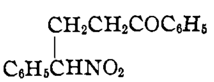
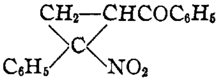
[10] Ref. 9, p. 975.

[1] Kohler, *Am. Chem. J.*, **42**, 375 (1909).

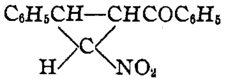
present in doubt. Thus, for example, from the addition product of phenylnitromethane (IV) it should be possible to make a nitrocyclopropane derivative (VII) isomeric with the one that is known (VIII), and a comparison of these isomers would be expected to yield valuable information on the mechanism of the peculiar rearrangements of these cyclopropane derivatives.



IV



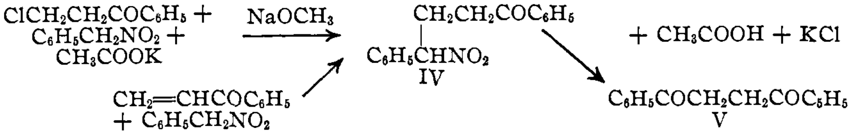
VII



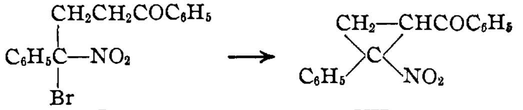
VIII

Unfortunately, the preparation of large amounts of vinyl phenyl ketone is so difficult[2] that it is not a serviceable starting material for any extensive investigations. It occurred to us that it might be possible to substitute the more readily available β-chloropropiophenone (III), and remove from it hydrogen chloride either just prior to use or in the presence of the substance to be added, thus avoiding isolation of the reactive unsaturated ketone. This procedure was, indeed, found to be possible.

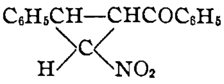
In the presence of alkaline reagents, phenylnitromethane combined with β-chloropropiophenone to give the same saturated γ-nitro-ketone (IV) as was obtained with phenyl vinyl ketone. Its structure was proved by the formation of dibenzoylethane (V) when a solution of the sodium derivative was decomposed with cold dilute hydrochloric acid.[3]



On bromination in a solution of sodium methylate, followed by elimination of hydrogen bromide, a tertiary nitrocyclopropanone (VII) was produced.



VI VII



VIII

The behavior of this compound with sodium methylate was of particular interest because the previous investigations[4] showed that if a secondary

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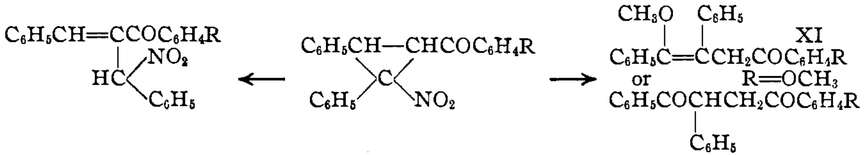
[2] (a) Van Marle and Tollens, *Ber.*, **36**, 1352 (1903); (b) Kohler, ref. 1, the only one to prepare any considerable quantity; (c) Beaufour, *Bull. soc. chim.* [IV] **13**, 356 (1913); (d) Straus, *Ann.*, **393**, 260 (1912); **401**, 142 (1913); (e) Norris and Couch, THIS JOURNAL, **42**, 2330 (1920); (f) Mannich, *Ber.*, **55**, 356 (1922).

[3] Nef, *Ann.*, **280**, 267 (1894).

[4] (a) Kohler and Engelbrecht, THIS JOURNAL, **41**, 1379 (1919); (b) Kohler and Williams, *ibid.*, **41**, 1644 (1919); (c) Kohler and Srinivasa Rao, *ibid.*, **41**, 1697 (1919); (d) Kohler and Smith, *ibid.*, **44**, 624 (1922); (e) Kohler and Paul Allen, *ibid.*, **50**, 884 (1928).

nitro group was present (VIII), the final product was a 1,3-diketone, while with a tertiary nitro group (IX) two types of reaction occurred, one forming an ethylenic compound with the nitro group still present and the other a nitrogen-free 1,4-diketone (or its monomethyl ether).


X IX XII

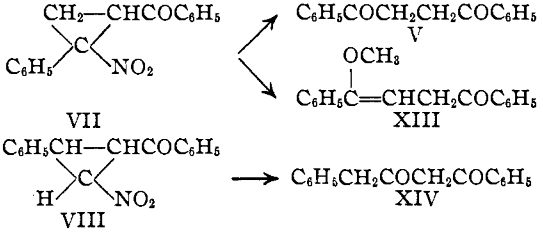
XI R=OCH₃

After separation of one of the two theoretically possible isomers of (VII), a lower-melting solid was deposited from the solution; this substance analyzed for an isomer, but was a constant-melting mixture undoubtedly containing some of the cyclopropane first isolated, since mixtures always gave melting points intermediate between those of this solid and the pure cyclopropane. All efforts to separate it into its constituents by fractional crystallization or change of solvents were unsuccessful.

Both this solid and the isomeric cyclopropane derivative reacted with sodium methylate, yielding dibenzoylethane (V) and its methyl ether (XIII).

The formation of dibenzoylethane can only be explained by the opening of the ring between carbon atoms 1 and 2—a new type of reaction between cyclopropane ketones and alkaline reagents. Those studied previously, chiefly by Kohler and his students, if attacked by bases, were always opened in the 1,3- or 2,3-positions. There is nothing novel about the ring being broken in different places by other reagents (*e. g.*, reducing agents have attacked all three possible bonds), but this is the first time that alkaline reagents have been found to react in the 1,2-position.

The isomeric nitrocyclopropanone (VIII)[4a] under similar conditions also opened between the carbon atoms to which the phenyl and benzoyl groups are respectively attached, and the final product is a 1,3-diketone (XIV).


VII V XIII VIII XIV

Experimental

The Addition Product with Phenylnitromethane

γ-Nitro-γ-phenylbutyrophenone (IV). A.—Fifteen grams of β-chloropropiophenone[5] and 12 g. of fused potassium acetate were dissolved in 60 cc. of hot methyl

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[5] Prepared by the method of Hale and Britton, THIS JOURNAL, **41**, 844 (1919).

alcohol. Then 12 g. of phenylnitromethane in 20 cc. of alcohol was added and the whole made faintly alkaline to litmus by admitting a 5% solution of sodium methylate, drop by drop. The reddish mixture was refluxed for forty minutes, then acidified with acetic acid and poured into 120 cc. of cold water. After several hours the precipitated addition product was filtered; the average yield of several preparations was 82%—this was true only when the phenylnitromethane was redistilled. For purification it was dissolved in 40 cc. of hot benzene and dried with calcium chloride; the clear solution was decanted, warmed slightly and petroleum ether added to incipient cloudiness. The addition product crystallized in clusters of needles which were filtered and washed until white with a 1:1 mixture of ether and petroleum ether. A second crop was secured by partial evaporation of the mother liquor. Further purification was effected by a similar treatment or by recrystallization from methyl alcohol. Analytical samples prepared by either method gave the same result.

γ-Nitro-γ-phenylbutyrophenone crystallizes in bunches of needles that melt at 72°. It is very soluble in all the usual organic solvents except petroleum ether. It tends to separate as an oil from solutions containing other substances.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6. Found: C, 71.3; H, 5.7.

We did not try to isolate the vinyl phenyl ketone (except in one instance, to see that it was formed) or determine the extent of its formation quantitatively. Since none of the acetate, which has previously been isolated,[2a] was found at any time, the reaction between the chloro ketone and potassium acetate is probably best represented as follows

$$ClCH_2CH_2COC_6H_5 + CH_3COOK = CH_2{=}CHCOC_6H_5 + CH_3COOH + KCl$$

B.—Vinyl phenyl ketone was prepared by the method described by Mannich.[2f] The yellow oil from the steam distillation was dissolved in ether, dried over calcium chloride and the solvent evaporated in a tared flask. This residual oil was used without further purification.

To 3.8 g. of the ketone was added 10 cc. of absolute methyl alcohol; most of it immediately polymerized to a white, insoluble mass. The whole was warmed and the clear solution decanted from the polymer into a clean flask. Two grams of phenylnitromethane was added, then enough dilute sodium methylate to give an alkaline reaction to litmus, and the mixture warmed on the steam-bath for fifteen minutes. It was next acidified with acetic acid; an oil separated and crystallized on cooling. This was purified as described above and identified as the same substance by a comparison of melting points, mixed melting points and solubilities.

Proof of Structure.—One gram of the addition product was dissolved in a slight excess of sodium methylate, 10 cc. of water added and the clear solution filtered into 25 cc. of cold, dilute (1:5) hydrochloric acid. The white precipitate thus formed was filtered and recrystallized from methyl alcohol; yield, 0.7 g., or 80%. It was identified as dibenzoylethane (V) by melting point and mixed melting point with an authentic sample.[6]

Bromination.—The nitro ketone was readily brominated in sodium methylate solution, the bromine replacing the hydrogen on the γ-carbon atom. Like many other compounds having a bromine atom and nitro group on the same carbon atom, this substance decomposed just above its melting point.[7] The reaction is not clean, but the principal product is 2,5-diphenyl-3-bromofuran.

γ-Bromo-γ-nitro-γ-phenylbutyrophenone (VI).—Ten and two-tenths grams of

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[6] Kindly supplied by Dr. R. E. Lutz.

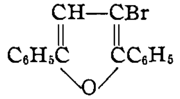
[7] Some of these compounds have been investigated by one of us; the results will appear in a subsequent paper.

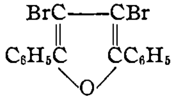
the nitro ketone was added to the sodium methylate solution prepared from 0.8 g. of sodium and 65 cc. of methyl alcohol, the whole being cooled in an ice-bath and well stirred. After ten minutes a slight excess over the theoretical amount of bromine was run in from a dropping funnel, the end of which was drawn out into a fine capillary. A white solid soon separated. The excess bromine was removed by sodium bisulfite solution, and the buff-colored precipitate filtered and thoroughly washed with water and alcohol; yield of crude solid, 94%. It was recrystallized rapidly from glacial acetic acid; prolonged heating resulted in decomposition. It formed long, fine prisms that melted at 146° with gas evolution. It is insoluble in petroleum ether, very slightly soluble in ether and the alcohols, moderately soluble in acetone, ethyl acetate and chloroform, but easily soluble in glacial acetic acid or pyridine; a solution in the latter solvent does not readily lose hydrogen bromide.

Anal. Calcd. for $C_{16}H_{14}O_3NBr$: Br, 22.7. Found: Br, 22.3.

After boiling for fifteen minutes with alcoholic sodium hydroxide and acidifying the solution, a 50% yield of dibenzoylethane résulted; the residue remained as an oil.

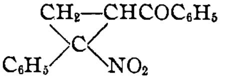
The Bromofurans,

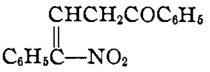


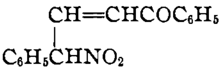


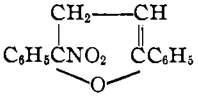
A solution of the bromonitro compound in glacial acetic acid was refluxed for an hour; oxides of nitrogen appeared in the condenser. The black solution was poured into water, the precipitated oil extracted with ether, the extract dried with calcium chloride and the solvent allowed to evaporate spontaneously. The oil left was then dissolved in methyl alcohol; on slow evaporation crystals separated; they melted at 76–77°, and on recrystallization at 77–78°. They were identified as 2,5-diphenyl-3-bromofuran by comparison with a sample at hand. A small amount of another solid was also isolated and identified as 2,5-diphenyl-3,4-dibromofuran, m. p. 88°.[6]

The Nitrocyclopropanones.—The bromo ketone loses hydrogen bromide very slowly in a boiling methyl alcoholic solution of potassium acetate, but prolonged heating gives a good yield of cyclopropane. By derivation, substances formed from (VI) by loss of hydrogen bromide could be cyclopropane derivatives (VII), ethylenic compounds (XV, XVI), or dihydrofuran derivatives (XVII), but since in all such previous instances only the cyclopropane has been formed, it would be expected here. Further, the products neither decolorize bromine nor reduce permanganate, thus excluding the ethylenic compounds (XV, XVI). Also, as furan rings are not sensitive to alkaline reagents, although the substance (XVII) could lose nitrous acid, the product expected would be the known 2,5-diphenylfuran.


VII


$C_6H_5C(NO_2){=}CHCH_2COC_6H_5$
XV


$C_6H_5CHNO_2{-}CH{=}CHCOC_6H_5$
XVI


XVII

1-Phenyl-1-nitro-2-benzoylcyclopropane (X).—Fifteen grams of the bromo compound and an equal weight of fused potassium acetate in 75 cc. of absolute methyl alcohol was refluxed for twenty-two hours. The solution was decanted from the bulk of the potassium bromide and the solvent partially evaporated. An oil separated on cooling, but soon solidified; the crude product was filtered; yield, 90%. It was submitted to fractional crystallization, using different solvents, in an effort to isolate both isomeric forms. Ethyl acetate gave the best separation; most of the high-melting cyclopropane crystallized out first, followed by a mixture of constant melting point. Attempts to separate this into its constituents were unsuccessful. Both the pure nitrocyclopropane and the mixture crystallized in rosets, made up of fine white needles, which dissolved easily in all the usual organic solvents except petroleum ether. The pure substance melts at 131° and the mixture at 80°. The analytical samples were crystallized from methyl alcohol.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.9; H, 4.9. Found: (131°) C, 71.7; H, 5.0; (80°) C, 71.7; H, 5.1.

The melting points of mixtures in several proportions of the pure nitrocyclopropane and the substance of constant melting point all were above that of the latter and below that of the former. Neither solid reduces permanganate nor decolorizes bromine. They may be recrystallized unchanged from acetyl chloride. On addition to concd. sulfuric acid, a bright green color was produced and oxides of nitrogen were evolved. This reaction is to be investigated.

Action of Sodium Methylate.—Five grams of the constant-melting substance was added to 40 cc. of 5% sodium methylate solution; on warming, the solid dissolved and solid sodium nitrite separated from the brown liquid. The latter was decanted into a separatory funnel containing 100 cc. of water and enough ether added to give two layers. The ether layer was separated and the aqueous layer extracted once. The combined ethereal solutions were washed with water, followed in order by solutions of sodium bicarbonate, copper acetate, potassium carbonate and water, and then dried over calcium chloride. On evaporation, 2.4 g. of yellow oil was left; it slowly deposited dibenzoylethane. The original aqueous layer was acidified, extracted with ether and the extract treated similarly. On evaporation it left 1.7 g. of an oil that deposited more dibenzoylethane during the course of a month. The total yield of diketone was 70%. Nothing was obtained from any of the solutions used to wash the ethereal extracts. When the operation was interrupted after five minutes, the first ether extract deposited high-melting nitrocyclopropane as well as dibenzoylethane.

The cyclopropane, m. p. 131°, behaved similarly, on the same treatment; 4.1 g. of oil was obtained. During the course of three weeks it slowly deposited 55% of the theoretical amount of dibenzoylethane and 10% of the theoretical amount of the monomethyl ether of that diketone (XIII). This was a very sensitive substance, difficult to recrystallize without hydrolysis to dibenzoylethane. It is very soluble in all the usual solvents; methyl alcohol gave fine, white needles, m. p. 72°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 81.0; H, 6.4. Found: C, 81.1; H, 6.3.

On cautious oxidation by permanganate the odor of methyl benzoate could be detected; benzoic acid was also identified.

A small portion of the oil was oxidized by permanganate; no benzaldehyde could be detected; the sole solid product was benzoic acid. A second portion failed to give a solid when treated with semicarbazide in the usual way.

This tertiary nitrocyclopropane is relatively inactive with hydrogen bromide. The mixed solid is turned into the high-melting form (131°) which does not react.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

We are indebted to Professor E. P. Kohler for valuable criticism in the preparation of this paper.

Summary

1. It has been shown that β-chloropropiophenone can be used in place of vinyl phenyl ketone in addition reactions. With phenylnitromethane the same γ-nitro ketone is obtained from both substances.

2. The nitro ketone is easily brominated in the gamma position; the bromo ketone is unstable to heat. Hydrogen bromide is eliminated by the use of potassium acetate, and the product is a tertiary nitrocyclopropanone.

3. Sodium methylate reacts with this cyclic nitro compound in such a way that the ultimate product is dibenzoylethane.

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[Contribution from the Chemistry Laboratory of the University of Michigan]

TRIARYLMETHYL CARBONATES. CATALYTIC DECOMPOSITION IN THE PRESENCE OF COPPER

By J. O. Halford

Received January 31, 1929 Published July 5, 1929

Triphenylmethyl carbonate has been recorded by Gomberg[1] as an intermediate in the preparation of triphenylmethyl oxide. The carbonate was formed by the action of silver carbonate on triphenylchloromethane in benzene

$$2(C_6H_5)_3CCl + Ag_2CO_3 = [(C_6H_5)_3C]_2CO_3 + 2AgCl \qquad (1)$$

A solution of triphenylmethyl carbonate in boiling xylene produced triphenylmethyl oxide and carbon dioxide under the catalytic influence of finely-divided copper.

$$[(C_6H_5)_3C]_2CO_3 \longrightarrow CO_2 + [(C_6H_5)_3C]_2O \qquad (2)$$

This reaction, similar to the thermal decomposition of metallic carbonates, is consistent with the general properties of the triarylmethyls, whose salts with strong acids, particularly the halides, show many of the reactions of metallic salts. If the analogy is complete, Equation 2 should represent a general reaction of the triarylmethyl carbonates and should be reversible.

With this in mind, three other carbonates, those of diphenyl-α-naphthylmethyl, *p*-tolyldiphenylmethyl and phenylbiphenylenemethyl, have been prepared and their behavior in the presence of copper powder studied. Although *p*-tolyldiphenylmethyl carbonate and diphenyl-α-naphthylmethyl carbonate are decomposed catalytically by copper, the oxides have not been obtained in appreciable quantity and it must be concluded that Reaction 2 is not general, but that the catalytic effect of copper is common to the triarylmethyl carbonates. The decomposition of triphenylmethyl carbonate has not been reversed.

Further, the occurrence of a slow catalytic decomposition presents an opportunity to study the mechanism through the interpretation of the rate of reaction. This has been done for the decomposition of triphenylmethyl carbonate.

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[1] Gomberg, This Journal, 35, 200 (1913).