[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Cyclopropanes. XVI. 1-*p*-Bromobenzoyl-2-nitro-3-phenylcyclopropane: Preparation and Action of Basic Reagents[1]

BY LEE IRVIN SMITH AND EARL D. HOLLY[2]

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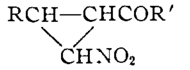
Three of the four possible racemic forms of the nitrocyclopropyl ketone I have been prepared and subjected separately to the action of various basic reagents. Ia, melting at 135.5–136°, could be converted into Ib, melting at 120.5–121°, or into Ic, melting at 166.5–167.5°; Ib could be converted into Ic. These conversions are not reversible. All three stereoisomers could be converted into 2,4-dinitrophenylhydrazones, but the rates were different and were in the order Ic > Ib > Ia. All three isomers gave the same enol ether or the same 1,3-diketone by action of aqueous or alcoholic alkali, and all three isomers gave the same pyrone by action of sodiomalonic ester. Except for the conversions of one stereoisomer into another, and the reactions with 2,4-dinitrophenylhydrazine, the reactions of the three isomers with bases show no significant differences.

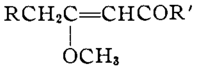
In continuation of the studies on the action of various reagents upon nitrocyclopropyl ketones, and the mechanism whereby these substances are converted into other cyclic compounds and into open chained compounds, an investigation of the chemistry of 1-*p*-bromobenzoyl-2-nitro-3-phenylcyclopropane (I) was undertaken. This nitrocyclopropane was chosen because the presence of the two phenyl groups, one of them marked by the *p*-bromine atom, might likely lead to decomposition products more readily characterizable than usual, and also because this nitrocyclopropyl ketone had been prepared and studied many years ago by Kohler and Williams[3] and some of the possible decomposition products were already known. The study of Kohler and Williams, however, was not extensive enough for our purpose and moreover these authors did not deal specifically with questions concerning the mechanism whereby the ring is opened.

The synthesis of I involved the usual sequence of reactions for preparation of these nitrocyclopropanes. Nitromethane was added to benzal-*p*-bromoacetophenone, producing the γ-nitro ketone VIII in 62% yield. Bromination in alkaline solution converted VIII into the dibromo compound IX (43%); the only by-product isolated was unchanged VIII.[4] The monobromo compound X could not be isolated, although it was undoubtedly present, because the crude bromination product could be converted into I in fair yield, whereas pure IX could not. The α-bromo ketone XI was formed in 70% yield by bromination of VIII in neutral solution. The diastereoisomers were not separated, and the analytical sample melted over a wide range; nevertheless, for preparation of I in quantity, this material was quite suitable. Action of alcoholic potassium iodide upon XI produced VIII, rather than the iodo ketone XII, as was reported by Kohler and Williams.[3]

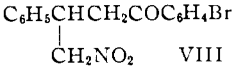


I, R = C_6H_5
R′ = p-BrC_6H_4-
III, R = R′ = C_6H_5
VI, R = C_6H_5
R′ = cyclopropyl
VII, R = cyclopropyl
R′ = C_6H_5

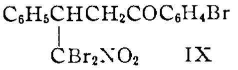
RCH_3COCH_2COR'
II, R = R′ = C_6H_5
XIV, R = C_6H_5
R′ = p-BrC_6H_4-



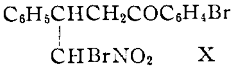
$\underset{\displaystyle OCH_3}{RCH_2C}{=}CHCOR'$



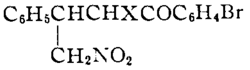
$\underset{\displaystyle CH_2NO_2}{C_6H_5CH}CH_2COC_6H_4Br$ VIII



$\underset{\displaystyle CBr_2NO_2}{C_6H_5CH}CH_2COC_6H_4Br$ IX

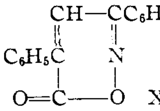


$\underset{\displaystyle CHBrNO_2}{C_6H_5CH}CH_2COC_6H_4Br$ X



$\underset{\displaystyle CH_2NO_2}{C_6H_5CH}CHXCOC_6H_4Br$

XI, X = Br
XII, X = I



XIII

IV, R = C_6H_5; R′ = cyclopropyl
V, R = cyclopropyl; R′ = C_6H_5
XV, R = C_6H_5; R′ = p-BrC_6H_4-

Three forms of the nitrocyclopropane, I, Ia, m.p. 135.5–136°; Ib, m.p. 120.5–121°; Ic, m.p. 166.5–167.5°, were obtained when the bromo compounds IX, X (not isolated) and XI were subjected to action of bases. Ic (36%) was formed by action of alcoholic potassium acetate upon impure X (containing IX and VIII); VIII (32%) was also recovered. Ic was also produced in small (3%) yield by action of the same reagent upon pure IX; in this case the reaction also involved a reductive removal of one of the bromine atoms.[4] The action of alcoholic potassium acetate upon the α-bromo ketone XI produced a mixture of Ia and Ib (86%). Ia and Ib were initially separated by chromatography upon a column of silica gel; after seed crystals were available, it was possible to seed a solution of the mixture in benzene–petroleum ether with Ia, crystallize this first, and then crystallize Ib from the filtrate. A fourth substance, melting at 143–145°, was obtained after all compound I had been removed. This substance was unstable and was transformed, upon crystallization from benzene–alcohol, into another substance melting at 176–177°. Both substances reduced potassium permanganate in acetone. Analysis of the second substance indicated that it might be 3-*p*-bromophenyl-5-phenyl-6-H-1,2-oxazin-6-one (XIII), a substance to be expected as a by-product in analogy with the work of Kohler.[5]

Either Ia and/or Ib were transformed (92%) into Ic by action of methanolic ammonia.[6] Ia was

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(1) Paper XV, L. I. Smith and Bob K. Davis, THIS JOURNAL, **76**, 5376 (1954).

(2) Abstracted from a thesis by Earl D. Holly, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, 1953. National Science Foundation Fellow, 1952–1953.

(3) E. P. Kohler and H. E. Williams, THIS JOURNAL, **41**, 1644 (1919).

(4) See also L. I. Smith and J. S. Showell, *J. Org. Chem.*, **17**, 836 (1952), for a similar case.

(5) E. P. Kohler, *et al.*, THIS JOURNAL, **46**, 503 (1924); **48**, 2425 (1926); **49**, 219 (1927); **50**, 221 (1928).

(6) E. P. Kohler and L. I. Smith, *ibid.*, **44**, 624 (1922).

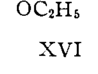
transformed into Ib (43%) by action of zinc dust in boiling aqueous alcohol; this reagent was without action upon Ib or Ic. It had previously been reported that I was reduced to VIII by action of this reagent.[3]

All three isomers of I were inert toward action of potassium permanganate in acetone, of potassium iodide in acetone or alcohol, and of bromine in carbon tetrachloride. All three isomers acted upon ferrous hydroxide, converting it into ferric hydroxide. The infrared spectra of Ia and Ib were very similar, but differed from that of Ic. All three spectra showed bands at 1675–1680 cm.^{-1} (conjugated carbonyl) and at 1535–1540 cm.^{-1} (nitro group). A strong Nujol band at 1365–1370 cm.^{-1} made detection of the band at 1335 cm.^{-1} (nitro group) difficult.

All three isomers of I could be converted into 2,4-dinitrophenylhydrazones, but the rates differed markedly. In 40 hours the yields were, respectively, 53, 60 and 95% from Ia, Ib and Ic; in 2.5 hours, the respective yields were 1, 21, and 63%.

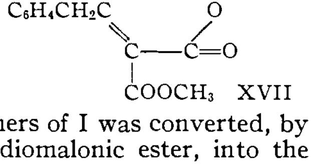
All three isomers of I were converted, by action of alcoholic sodium hydroxide, into the same 1,3-diketone XIV, melting at 80–80.5°, in yields of 27–33%. The copper enolate of XIV melted at 224–227° dec. This result parallels that of Kohler and Engelbrecht[7] who found that the three isomers of the cyclopropane III were all converted, by action of alkali, into the same 1,3-diketone II, although the yields of II were not the same from each of the isomers of III.

By action of methanolic sodium methoxide, all three isomers of I were converted into the same enol ether XV in yields of 21–30%. This result likewise parallels that of previous work; thus, the same enol ethers IV and V, respectively, were obtained from the stereoisomeric pairs of cyclopropanes VI and VII.[8] The analytical values of XV were erratic, as is frequently the case with these compounds, but action of hydrochloric acid upon XV converted it into the diketone XIV (38%). The ultraviolet absorption spectrum of XV showed a maximum at 286 mμ (ε 21,000), and a shoulder at 259 mμ (ε 4100)—corresponding with the *p*-bromobenzoyl group—this absorption was shown in the spectra of most of the compounds described in the present study. The absorption at 286 mμ arises from the double bond in XV, for the enol ether XVI gives a spectrum which also shows this absorption (284 mμ, ε 33000)[9] and the location of the double bond in XV has been definitely settled by oxidation of XV to methyl phenylacetate and *p*-bromobenzoic acid.[3]



$$\underset{\displaystyle OC_2H_5}{CH_3\overset{}{C}}{=}CHCOC_6H_5$$

XVI



XVII

Each of the stereoisomers of I was converted, by action of methanolic sodiomalonic ester, into the same pyrone XVII, though in poor yields (2.5–10%). As a by-product, small amounts of the enol ether XV were formed, a result which has been observed before.[10]

The results reported herein show no great differences in the behavior of the stereoisomers of I toward basic reagents, except for the transformation of one isomer into another, brought about by weakly basic reagents which left the cyclopropane ring intact.

Experimental Part[11]

4-Nitro-3-phenyl-1-*p*-bromophenyl-1-butanone (VIII).—Nitromethane (33 ml., 37.5 g., 0.615 mole) was added with vigorous shaking (to avoid formation of lumps) to a solution of sodium (12.5 g., 0.54 mole) in 95% alcohol (190 ml.). The thick suspension of the sodium salt was added in one portion to a warm (60°) suspension of benzal-*p*-bromoacetophenone (143.5 g., 0.50 mole) in 95% alcohol (375 ml.). After the exothermic reaction subsided, the mixture was boiled on the steam-bath until all solids dissolved (about ten minutes) then cooled in an ice-bath. A mixture of glacial acetic acid (33 ml., 0.56 mole) and alcohol (100 ml.) was added dropwise with vigorous stirring to the cold (3–5°) solution. The solution was seeded occasionally with VIII; crystallization started when about half of the acid had been added. Acid was then added somewhat more rapidly until the reaction mixture was slightly acidic (*p*H 6). The solid was removed within minutes (important) and washed with alcohol, then with water. After one crystallization from alcohol, the product (107.4 g., 62%) melted at 101–102.5° (literature 101–102°[3]).

It is essential that the product not separate as an oil during the acidification, otherwise a very difficultly separable mixture of VIII and the termolecular product results.

The ultraviolet absorption spectrum of VIII (3.30×10^{-5} *M* in U. S. P. 95% ethanol) had a maximum (attributed to the 4-bromobenzoyl group) at 257 mμ, ε 18,000.

4-Bromo-4-nitro-1-*p*-bromophenyl-1-butanone (X) was never obtained in a pure state. In a procedure similar to that of Smith and Engelhardt,[12] powdered VIII (31.5 g., 0.09 mole) was added to a cooled (Dry Ice) solution of sodium (2.3 g., 0.10 mole) in methanol (80 ml.). The resulting suspension was added, with stirring, to a cooled (Dry Ice) solution of bromine (5.5 ml., 16.6 g., 0.104 mole) in chloroform (150 ml.). The cooling bath was removed and stirring was continued for 35 minutes. The reaction mixture was extracted successively with aqueous sodium bisulfite and with water, then dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue, crystallized from alcohol–benzene, yielded three crops of yellow material (30.63 g.), melting 83–94°. Recrystallization of each crop gave a white product; after four crystallizations a sample melted at 97–103°. Analysis indicated that it was chiefly unbrominated VIII and the melting point of a mixture with VIII was undepressed. Formation of iodine and potassium bromide when the substance was subjected to the action of potassium iodide in acetone, however, indicated that some X might be present.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_2$ (X): C, 45.00; H, 3.07. Calcd. for $C_{16}H_{14}NO_3Br$ (VIII): C, 55.19; H, 4.05. Found: C, 54.36; H, 4.31.

The experiment was repeated except that the amount of bromine used was just equivalent to the VIII (5 g.). The product (4 g.) melted at 72–127°; after four recrystallizations from alcohol–benzene, it melted at 134–139°. Analysis indicated that it was chiefly IX.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_3$ (IX): C, 37.98; H, 2.39. Found: C, 40.90; H, 2.89.

4,4-Dibromo-4-nitro-1-*p*-bromophenyl-1-butanone (IX).—In a third experiment, the methanolic suspension of the sodium salt of VIII (16 g., 0.046 mole) was added to a solution

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(7) E. P. Kohler and H. F. Engelbrecht, THIS JOURNAL, **41**, 1379 (1919); see also E. P. Kohler, *ibid.*, **50**, 221 (1928).

(8) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3831, 3837 (1951).

(9) R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934).

(10) L. I. Smith and R. E. Kelly, THIS JOURNAL, **74**, 3300 (1952).

(11) Microanalyses were carried out in the microlaboratory of the Department of Chemistry, and the spectral data were determined in the Spectrographic Laboratory of the Department of Chemistry, University of Minnesota.

(12) L. I. Smith and V. A. Engelhardt, THIS JOURNAL, **71**, 2676 (1949).

of excess bromine in chloroform. The product was IX (10 g., 43%) melting at 137–141°; after four recrystallizations from alcohol–benzene the substance melted at 146–147°.

Anal. Calcd. for $C_{16}H_{12}NO_3Br_3$: C, 37.98; H, 2.39. Found: C, 37.79; H, 2.62.

2-Bromo-4-nitro-1-*p*-bromophenyl-1-butanone (XI).—A small amount of bromine was added to a solution of VIII (20 g., 0.058 mole) in chloroform (150 ml.), and the bromination was started by heating the mixture on the steam-bath until sudden, vigorous boiling occurred, accompanied by fading of the color. The solution was then cooled and the remainder of the bromine (3.4 ml., 9.6 g., 0.06 mole) was added. The solvent was removed under reduced pressure; the residual yellow oil partially crystallized in contact with cold methanol. A solution of the material in hot methanol, when cooled, deposited a white solid (8.4 g., 34%) melting at 78–80°. Recrystallization gave a first crop (6.49 g.) melting at 84–95° and a second crop (1.44 g.) melting at 85–103°. More product (8.70 g., 36%), melting at 74–95°, slowly separated from the original methanolic solution.

The two stereoisomers of XI were not readily separated by crystallization. After eight crystallizations, XI melted at 110–117°.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_2$: C, 45.00; H, 3.07. Found: C, 45.03; H, 3.33.

For preparation of I in quantity, the crude XI was used directly after removal of the chloroform.

Action of Potassium Iodide upon XI.—A solution of XI (1.44 g., 0.0034 mole) and potassium iodide (1.5 g.) in absolute alcohol (25 ml.) was boiled for 30 minutes, cooled, and poured into aqueous sodium thiosulfate. The solid was separated, washed with water, dried, and recrystallized twice from alcohol. The product was VIII, m.p. and mixed m.p. 105.5–106°.

Anal. Calcd. for $C_{16}H_{14}NO_3Br$: C, 55.19; H, 4.05. Found: C, 55.65, 55.50; H, 4.32, 4.23.

1-*p*-Bromobenzoyl-2-nitro-3-phenylcyclopropane (I). (a) **From IX.**—A suspension of IX (7.8 g., 0.0154 mole) and potassium acetate (8 g.) in absolute alcohol (25 ml.) was boiled for 15 minutes, then left for 16 hours at room temperature. The mixture was poured into water, the solid was removed, washed with water, then crystallized from alcohol-benzene. There resulted yellow aggregates of needles plus an oil. The crystals were separated mechanically from the oil and recrystallized from alcohol–benzene. Fine, white needles of Ic (0.16 g., 3%) melting at 156–167° were obtained. When recrystallized, they melted at 165–166.5°.

(b) **From X.**—Impure X (10 g., 0.0234 mole) was subjected to the action of potassium acetate (12 g.) in absolute alcohol (150 ml.). The mixture was heated to the boiling point, then allowed to cool. The solid was removed and fractionally crystallized from alcohol. There resulted impure Ic (3.41 g., 44%) melting at 152–164° and VIII (2.65 g., 32%, probably present originally in the impure X used) melting at 100–101°. After crystallization from alcohol, Ic melted at 165–166° (2.99 g., 36%).

(c) **From XI.**—A suspension of XI (6.49 g., 0.152 mole) and freshly fused potassium acetate (4 g.) in absolute alcohol (30 ml.) was boiled for *five* minutes, then cooled. The solid was removed, washed with alcohol–water (10 ml., 1:1) and then with water until free of bromide ion. The crude I (4.52 g., 86%) melted at 80–86°; this product could not be separated into the pure stereoisomers by crystallization from alcohol–benzene. Samples melting at 118–121° and at 124–132° were analyzed.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 55.90, 55.67; H, 3.67, 3.61.

By-products of the Action of Potassium Acetate upon XI.—After removal of Ia and Ib, the alcoholic filtrate, on long standing, deposited shiny tan plates which melted at 143–145° and reduced potassium permanganate in acetone. When recrystallized from alcohol–benzene, it was transformed into a second substance melting at 176–177°, which crystallized as shiny white plates and reduced potassium permanganate in acetone. This material, probably the 1,2-oxazinone XIII,[5] became green when exposed to light.

Anal. Calcd. for $C_{16}H_{10}NO_2Br$: C, 58.54; H, 3.07. Found: C, 58.36; H, 3.30.

The separation of Ia from Ib was initially effected by chromatography of the solution of the mixture of isomers (obtained from XI) in 1:1 benzene–petroleum ether (b.p. 60–68°) on a column of silica gel (100–200 times the weight of the I). I was eluted with benzene–petroleum ether as the benzene content of the solvent was gradually increased (1:1, 3:2, 2:1, then 4:1). Ia, melting at 135.5–136°, was obtained first, followed by Ib, melting at 120.5–121°. Each stereoisomer was shown to be homogeneous by chromatography.

Having the pure stereoisomers for seeds, it was possible in subsequent experiments to crystallize first Ia, then to crystallize Ib from the filtrate. Ia was obtained in the greater quantity.

Transformation of Ia into Ib.—In an attempt to reduce Ia to VIII, a solution of Ia in 80% alcohol was boiled with zinc dust.[3] The product was Ib (43%) melting at 116–119°; no VIII was obtained. A mixture of this product with pure Ib melted at 117–120°. Both Ib and Ic were recovered unchanged when solutions of them in 80% alcohol were boiled with zinc dust.

Transformation of Ia and Ib into Ic.—A mixture of Ia with Ib (42 g.), melting at 129–136°, was suspended in absolute methanol (150 ml.) previously saturated with anhydrous ammonia.[6] After three days, the solid was separated. It was Ic (38.81 g., 92%) melting at 162–164.5°. The analytical sample, crystallized from benzene–petroleum ether (b.p. 60–68°), melted at 166.5–167.5°.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 55.36; H, 3.51.

On one occasion, when the low-melting stereoisomers were recrystallized from alcohol–benzene, spontaneous isomerization to Ic occurred. In a later experiment, when hydrogen chloride was added to Ib in glacial acetic acid, about 10% of the Ib was converted into Ic (which did not react with hydrogen chloride). For preparation of Ic in quantity, the mixture of Ia with Ib was prepared from XI and isomerized to Ic by action of methanolic ammonia.

Properties of I.—All three stereoisomers of I were unchanged by the action of potassium permanganate in acetone, of bromine in carbon tetrachloride, and of potassium iodide in alcohol or acetone. All three isomers oxidized ferrous hydroxide to ferric hydroxide (test for nitro group). The ultraviolet absorption spectrum of a mixture of Ia with Ib (2.10×10^{-5} *M* in U.S.P. 95% ethanol) showed a maximum at 260–261 mμ, ε 18,800. Ic (2.19×10^{-5} *M*) showed a maximum at 264 mμ, ε 21,700. The infrared absorption spectra of the isomers were obtained using Nujol mulls. The spectra of Ia and Ib were remarkably similar, but differed from that of Ic. All three spectra showed bands at 1675–1680 cm.$^{-1}$ (resulting from the conjugated carbonyl group) and at 1535–1540 cm.$^{-1}$ (resulting from the nitro group). A strong Nujol band at 1365–1370 cm.$^{-1}$ made uncertain detection of the band at about 1335 cm.$^{-1}$ to be expected from the nitro group.

The 2,4-dinitrophenylhydrazones of the stereoisomers of I were made by the method given in Shriner and Fuson[13] with the modification that more alcohol (70 ml., hot) was required to dissolve the I. The freshly prepared reagent was added to the hot solution of each stereoisomer of I (0.5 g.) in alcohol and the reaction mixture was left at room temperature for 40 hours. The precipitate was separated and washed with alcohol. The orange derivative of Ia (0.40 g., 53%) melted at 175–179° (dec.), and was contaminated with unchanged Ia. The yellow derivative of Ib (0.46 g., 60%) melted at 182–183° dec.; the filtrate contained unchanged Ib. The yellow derivative of Ic (0.72 g., 95%) melted at 195–197° dec.

The experiment was repeated, but the derivatives were separated after only 2.5 hours. The derivative of Ia (0.01 g., 1%) melted at 183.5–185.5° dec. The derivative of Ib (0.16 g., 21%) melted at 188–192° dec. The derivative of Ic (0.48 g., 63%) melted at 192–194° dec.

The 2,4-dinitrophenylhydrazones were recrystallized from chloroform, then from alcohol–ethyl acetate. The orange plates derived from Ia melted at 187–189° dec.; the yellow needles derived from Ib melted at 193–194° dec.; and the yellow needles derived from Ic melted at 193.5–195° dec. The ultraviolet spectra of the three derivatives were determined somewhat into the visible region; minor differences

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[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Third Edition, 1948, p. 171.

in the spectra indicated that the derivatives were not identical.

Anal. Calcd. for $C_{22}H_{16}N_5O_6Br$: C, 50.21; H, 3.07. Found: C, 50.50; H, 3.60; C, 50.61; H, 3.37; and C, 49.45; H, 3.29; for the derivatives of Ia, Ib and Ic, respectively.

4-Phenyl-1-*p*-bromophenyl-1,3-butandione, XIV, and its Copper Enolate.—Ia (1 g., 0.0029 mole) was added to a solution of sodium hydroxide (2 g.) in 95% alcohol (40 ml.). The red mixture was left at room temperature overnight, then poured into ice-water, acidified with dilute sulfuric acid, and extracted with ether. The ether extract was shaken with saturated aqueous cupric acetate, and the green cupric enolate was separated and washed with ether and with water. The enolate, melting at 224–227° dec., was shaken with a mixture of ether and dilute hydrochloric acid. The ether layer was washed with water, dried ($MgSO_4$), and concentrated. The orange residue of XIV crystallized from methanol as light orange plates (0.25 g., 27%) melting at 79–81°.

In an identical experiment, Ib was converted into XIV (0.30 g., 33%) melting at 77–80°. The enolate (0.30 g., 30%), melting at 224–227° dec., was obtained from an identical experiment with Ic, but a portion of the material was lost so that the yield of XIV (0.11 g., 12%), melting at 79.5–80°, was lower. The melting points of the samples of XIV obtained in these experiments were undepressed when mixed with the light tan analytical sample, melting at 80–80.5°, obtained from a mixture of Ia and Ib.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.57; H, 4.13. Found: C, 60.58; H, 4.35.

3-Methoxy-4-phenyl-1-*p*-bromophenyl-2-buten-1-one (XV).—In separate experiments, methanolic sodium methoxide (30 ml., 1 *N*) was added to each stereoisomer of I (1 g., 0.0029 mole), and the mixture was left at room temperature for one day. The red solution was poured into ice-water (160 g.) and extracted with ether (three 40-ml. portions). The combined ether extracts were washed with 5% aqueous sodium bicarbonate (50 ml.), then with water (two 70-ml. portions). The ether solution was dried ($MgSO_4$) and the solvent was removed. The residue was crystallized from absolute methanol. Thick orange needles of XV (0.20 g., 20%; 0.29 g., 30%; and 0.25 g., 26% from Ia, Ib and Ic, respectively) melting at 102.5–103.5° were obtained after two recrystallizations from absolute methanol. The analytical values were erratic.

Anal. Calcd. for $C_{17}H_{15}O_2Br$: C, 61.64; H, 4.57. Found: (melting at 103–104°) C, 60.90; H, 4.82; and (melting at 103.5–104.5°): C, 61.77; H, 5.25.

The ultraviolet absorption spectrum (2.85×10^{-5} *M* in U.S.P. 95% ethanol) of the second analytical sample showed a maximum at 286 mμ, ϵ 21,000; there was a shoulder on the curve; by extrapolation of the main absorption through this shoulder and subtraction, there remained a second maximum at 259 mμ, ϵ 4,100.

Hydrolysis of the Enol Ether XV to the Diketone XIV.—XV (0.20 g., 0.0006 mole) was dissolved in boiling methanol (10 ml.), and concd. hydrochloric acid (5 drops) was added. The solution was boiled for one hour, then poured into water (75 ml.) and extracted with ether (two 10-ml. portions). The ether extract was washed with water, dried ($MgSO_4$), and evaporated. The residue crystallized from methanol as light tan plates (0.07 g., 38%) melting at 79.5–80°. The melting point of a mixture with the analytical sample of XIV was the same.

3-Carbomethoxy-4-benzyl-6-*p*-bromophenyl-2-pyrone (XVII).—To a boiling solution of sodium (0.60 g., 0.026 mole) and dimethyl malonate (3.96 g., 0.030 mole) in absolute methanol (160 ml.), Ic (3.46 g., 0.010 mole) was added. The solution was refluxed for 1.5 hours, then set aside overnight at room temperature. It was then acidified with acetic acid to *p*H 6, and concentrated. The product, initially as an oil, later solidified. An analytical sample of XVII (0.12 g., 2.5%) melting at 146–148° was prepared by three recrystallizations from methanol.

Anal. Calcd. for $C_{20}H_{15}O_4Br$: C, 60.17; H, 3.79. Found: C, 59.90; H, 3.83.

The residues from the crystallization of XVII were dissolved in benzene and the solution was passed through a small chromatographic column packed with magnesium trisilicate–Hy-Flo. The most mobile component (0.15 g.), melting at 95–99°, was isolated. After three recrystallizations from methanol, the substance (0.07 g.) melted at 99.5–104°; the melting point of a mixture with XV was undepressed.

Anal. Calcd. for $C_{17}H_{15}O_2Br$: C, 61.64; H, 4.57. Found: C, 60.70; H, 5.32.

XVII was also made from Ia and from Ib by the above procedure. XVII (0.12 g., 10%) obtained from 1 g. of Ia melted at 143–145.5°; that (0.05 g., 4%) from 1 g. of Ib melted at 144–147°. Melting points of mixtures with the analytical sample of XVII were undepressed.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Cyclopropanes. XVII. 1-*p*-Bromobenzoyl-2-nitro-3-phenylcyclopropane: Action of Acidic Reagents[1]

BY LEE IRVIN SMITH AND EARL D. HOLLY[2]

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The three stereoisomers of the nitrocyclopropane I have been subjected to the action of hydrogen bromide, hydrogen chloride and bromine. Contrary to their behavior toward alkaline reagents, the three stereoisomers of I behave differently toward these acidic reagents and either give stereoisomeric adducts or two of them give stereoisomeric adducts and the third does not react. A study has been made of the stereoisomeric adducts and their transformation products, and several discrepancies between this work and the earlier work of Kohler and Williams have been noted.

In the previous paper[1] the action of basic reagents upon the three stereoisomers of 1-*p*-bromobenzoyl-2-nitro-3-phenylcyclopropane (I) was reported. The present paper deals with the action of acidic reagents upon these cyclopropanes and reports results which are at considerable variance with the results reported by Kohler and Williams,[3] who first prepared and studied cyclopropane I. The three stereoisomers of I are: Ia, melting at 135.5–136°; Ib, melting at 120.5–121°; and Ic, melting at 166.5–167.5°.

When Ia or Ib was dissolved in acetic acid, and hydrogen bromide was passed into the solution, the same adduct XIXa,[4] melting at 133–134.5° dec., was produced, in yields of 64 and 12%, respectively. When Ia or Ib was added to a saturated solution of

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[1] Paper XVI, THIS JOURNAL, **78**, 1472 (1956).

[2] Abstracted from a thesis by Earl D. Holly, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, 1953. National Science Foundation Fellow, 1952–1953.

[3] E. P. Kohler and H. E. Williams, THIS JOURNAL, **41**, 1644 (1919).

[4] The numbering of the compounds in this paper, and the preceding and succeeding ones, is arranged so that the numbers refer to the same compounds in all three papers.