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]

RECEIVED SEPTEMBER 23, 1955

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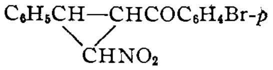
[1] Paper XVI, THIS JOURNAL, **78**, 1472 (1956).

[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).

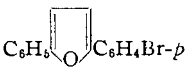
[4] The numbering of the compounds in this paper, and the preceding and succeeding ones, is arranged so that the numbers refer to the same compounds in all three papers.



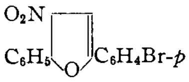
Ia, m.p. 135.5–136°
Ib, m.p. 120.5–121°
Ic, m.p. 166.5–167.5°

$C_6H_5CHCHNO_2CH_2COC_6H_4Br$-*p*

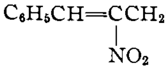
XIXa, X = Br, m.p. 133–134.5° dec.
XIXb, X = Br, m.p. 170–174° dec.
XXVII, X = Cl, m.p. 134–135° dec.



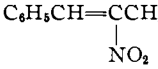
XVIII



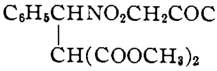
XXI



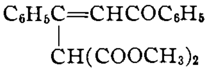
$C_6H_5CH{=}C(NO_2)CH_2COC_6H_4Br$-*p* XX



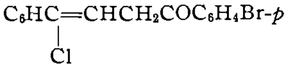
$C_6H_5CH{=}C(NO_2)CH_2COC_2H_5$ XXII



$C_6H_5CH(CH(COOCH_3)_2)NO_2CH_2COC_6H_5$ XXIII



$C_6H_5C(CH(COOCH_3)_2){=}CHCOC_6H_5$ XXIV

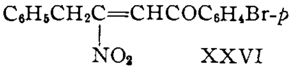


$C_6HC(Cl){=}CHCH_2COC_6H_4Br$-*p*

XXVIIIa, (?), m.p. 183–184°
XXVIIIb, m.p. 132.5–133°

$C_6H_5CHBrCHNO_2CHBrCOC_6H_4Br$-*p*

XXVa, m.p. 142–143° dec.
XXVb, m.p. 168–169° dec.



$C_6H_5CH_2C(NO_2){=}CHCOC_6H_4Br$-*p* XXVI

hydrogen bromide in acetic acid, the product was likewise XIXa in yields of 16 and 18%, respectively. When hydrogen bromide was passed into a solution of Ic in acetic acid, the product (14%) was the stereoisomeric adduct XIXb melting at 170–174° dec. When Ic was added to a solution of hydrogen bromide in acetic acid, no XIX could be isolated. Instead, the products were unchanged Ic (84.5%) and, when the solution was heated, a substance melting at 154–156° dec. which no longer contained nitrogen. Kohler and Williams reported that when Ia or Ic was added to acetic acid previously saturated with hydrogen bromide, the cyclopropane dissolved rapidly and the first adduct, melting at 144° dec. separated almost at once; when a solution of Ia or Ic in acetic acid was slowly saturated at 0° with hydrogen bromide and then left standing for 12 hours, the second adduct separated in long needles melting at 133°. They reported that both of their adducts were converted into the furan XVIII, melting at 127°, by action of boiling alcohol.

Of our adducts, XIXa was converted into this furan, m.p. 127–129°, by action of boiling alcohol, but action of this reagent upon XIXb produced no furan. Instead, the products were unchanged XIXb (23%) and the unsaturated nitro ketone XX (12%). Kohler and Williams reported that their adduct (they did not say which one) was converted by action of alcoholic potassium acetate into a dehydrobromination product melting at 162–163° dec. to which they assigned structure XX, without any proof, even though the analytical values were not in good agreement for XX. Our adduct XIXa was converted, by action of alcoholic potassium acetate, into a dehydrobromination product XXI melting at 167–168° dec. (28%), which reduced permanganate in acetone. The ultraviolet spectrum of XXI showed a single maximum at 267 mμ (ε 23000). Thermal decomposition of XXI gave XVIII (5%) which sublimed away from the main product, a dark tar. Ozonolysis of XXI produced *p*-bromobenzoic acid (95%) together with an unstable neutral substance which was not identified. XXI was unchanged by action of sodiomalonic ester, and also failed to react with 2,4-dinitrophenylhydrazine. On the basis of these facts, and although the analytical values for carbon were 0.65% high, XXI was assigned the structure of a dihydronitrofuran rather than structure XX, assuming that the substance melting at 162–163° dec. obtained by Kohler and Williams is identical with our substance melting at 167–168° dec.

Action of alcoholic potassium acetate upon XIXb produced a different dehydrobromination product XX, melting at 117–118° (60%), which reduced permanganate in acetone. The absorption of XX in the ultraviolet was roughly the sum of the absorptions of the *p*-bromobenzoyl group and of β-nitro-β-methylstyrene. There was a maximum at 259 mμ (ε 24,000), and a shoulder in the 300-mμ region. The *p*-bromobenzoyl group, in other compounds, produced a maximum at 257 to 264 mμ. When this absorption was subtracted from the spectrum of XX, a broad maximum at 300–310 mμ (ε 7500) remained. The maximum for β-nitro-β-methylstyrene is at 306 mμ. Compound XXII shows a maximum at 243 mμ (benzoyl group) and a broad maximum at 298–308 mμ.[5] Ozonolysis of XX produced *p*-bromoacetophenone, a small amount of *p*-bromobenzoic acid, a trace of benzoic acid and an aldehyde which was not identified. XX reacted with sodiomalonic ester, but the product could not be obtained pure.[6]

The bromine adducts XXVa and XXVb of Ia and Ib were produced when hydrogen bromide was passed into a cold solution of the mixed cyclopropanes and bromine in acetic acid (yield up to 56%). The two diastereomers were separated by fractional crystallization; XXVa crystallized from chloroform–petroleum ether as white rhomboids or short hexagonal prisms melting at 142–143° dec. XXVb crystallized from the same solvent as white needles melting at 168–169° dec. In one experiment, the intermediate XIXa (16%) was isolated, and XXVa (6%) and XXVb (63%) could be obtained by bromination of XIXa under the conditions used for bromination of I. Attempts to prepare a bromine adduct from Ic were unsuccessful; the products were unchanged Ic and the hydrogen bromide adduct XIXb. Nor could XIXb itself be brominated to XXV; unchanged XIXb was recovered (70%) although in one experiment a substance melting at 129–132° resulted in about 25% yield. This material appeared to result from replacement of the nitro group by bromine and no further work was done with it.

Kohler and Williams[3] reported that the unsaturated nitroketone XXVI, melting at 115°, was produced by action of potassium iodide in acetone upon XXVb, and, indeed, the preparation and study of XXVI had been one of the objects of the present series of investigations for XXVI is a likely precursor of the pyrones found by action of sodiomalo-

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

(6) See ref. 5 for reaction of XXII with sodiomalonic ester to give XXIII and XXIV.

nic ester upon nitrocyclopropyl ketones. It was found, however, that the chief product of this reaction of XXVb, which melted at 117.5–118° and presumably was identical with the substance melting at 115° obtained by Kohler and Williams, was not XXVI but actually was the isomeric substance XX. From XXVa also, impure XX (31%) melting at 97–115.5° was produced. One recrystallization of this impure material gave pure XX, m.p. and mixed m.p. 117.5–118°. Along with XX, there were produced from XXVa a white solid melting at 242–244°, a white solid melting at 128–130°, and a light yellow solid melting at 95–97°. The analytical values for the 128° material suggested that it had the same composition as the 1,3-diketone XIV (previous paper) and hence might be a 1,4-diketone. However, it could not be transformed into the furan XVIII by action of acid. The analytical values for the 95° material suggested that it might be XXVI, but no pure product could be isolated when the substance reacted with sodiomalonic ester.

Kohler and Williams reported that the hydrogen chloride adduct XXVII melting at 133°, was formed almost quantitatively by action of alcoholic hydrogen chloride upon Ia. This adduct, boiled with alcohol, was converted into the furan XVIII. Further, XXVII, by action of alcoholic potassium acetate, was converted into a mixture of the two stereoisomers of the chloroölefin XXVIII melting, respectively, at 179–180° and at 108–109°.

Our results were different in several respects. Action of hydrogen chloride in acetic acid upon either Ia or Ib produced XXVII, melting at 134–135° dec., in respective yields of 32 and 19%. XXVII had the required analytical values, and was converted into the furan XVIII by action of boiling alcohol. Ic was recovered unchanged (84%) after action of hydrogen chloride, either in dry ethanol or in acetic acid at 0°, room temperature, or 80°. When Ia reacted with hydrogen chloride in acetic acid, there was isolated, as a second crop of solid material, a substance (51%) melting at 111–112° which showed the required analytical values for a 1:1 complex of XXVII and XXVIIIb. This material slowly reduced permanganate in acetone, and probably was identical with the 108–109° substance assigned structure XXVIII by Kohler and Williams, who give analytical values for carbon 0.9% high for XXVIII. When Ib reacted with hydrogen chloride in acetic acid, it was partly isomerized into Ic (12%) which was isolated.

Action of alcoholic potassium acetate upon XXVII resulted in two products, XXVIIIa (12%) melting at 183–184°, and a small amount of XXVIIIb, melting at 132°. Our XXVIIIa was perhaps identical with the 179–180° compound of Kohler and Williams, but our analytical values for XXVIIIa were very poor and the structure of this compound is open to question. It reduced potassium permanganate in acetone, and gave no reaction with alcoholic silver nitrate. The ultraviolet spectrum showed a maximum at 265 mμ (ε 22,500). XXVIIIb was best prepared by action of alcoholic potassium acetate upon the 1:1 complex with XXVII. The yield was 40% and the product, melting at 132.5–133°, had the required analytical values, slowly reduced permanganate in acetone, and gave no reaction with alcoholic silver nitrate.

Experimental Part[7]

3-Nitro-4-bromo-4-phenyl-1-*p*-bromophenyl-1-butanone (XIXa), M.p. 133–134.5° dec.—A. Anhydrous hydrogen bromide was passed into a cooled solution of Ia (or Ib) (5 g., 0.0145 mole) in glacial acetic acid (200 ml.) for three hours. The solution was then left at 0° for five days and was then poured into ice-water (800 g.). The solid was separated, dissolved in chloroform, and the chloroform solution was washed with water, dried ($MgSO_4$) and concentrated somewhat. Sufficient petroleum ether (b.p. 60–68°) was then added to bring about crystallization as the solution cooled. XIXa (3.96 g., 64%) melting at 131.5–135° dec. was obtained from Ia. XIXa (0.73 g., 12%) melting at 130–134.5° dec. was obtained from Ib, as the solution was inadvertently allowed to become warm during the addition of the hydrogen bromide. The melting points of mixtures of these products with the analytical sample of XIXa were undepressed. The analytical sample, melting at 133–134.5° dec., had been prepared from a mixture of Ia with Ib.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_2$: C, 45.00; H, 3.07. Found: C, 45.79, 44.86; H, 3.17, 3.35.

B. A rapid stream of hydrogen bromide was passed for three hours into glacial acetic acid (250 ml.) cooled in an ice-bath; compound I (1 g., 0.0029 mole) was then added. After 15 hours all the I had dissolved and XIX was isolated as in A. Ia gave XIXa (0.20 g., 16%) melting at 131–133° dec.; Ib gave XIXa (0.22 g., 18%) melting at 127–129° dec. The melting points of mixtures with XIXa from A were undepressed

3-Nitro-4-bromo-4-phenyl-1-*p*-bromophenyl-1-butanone (XIXb), M.p. 170–174° dec.—A. Ic (10 g., 0.029 mole) was dissolved in glacial acetic acid (750 ml.), and hydrogen bromide was passed into the cooled (ice-bath) solution for four hours. The solution was left for one day at room temperature and then was poured into ice-water (2 kg.). The product was isolated as in the previous experiment. The XIXb (1.75 g., 14%) melted at 169–174° dec. The analytical sample, recrystallized from benzene–petroleum ether (b.p. 60–68°), melted at 170–174° dec. No other pure substance could be isolated.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_2$: C, 45.00; H, 3.07. Found: C, 45.43, 45.03; H, 3.20, 3.05.

The ultraviolet absorption spectrum (3.10×10^{-5} *M* in U.S.P. 95% ethanol) showed a maximum at 259 mμ, ε 20,400.

B. Ic (1.80 g., 0.0052 mole) was added to a solution of hydrogen bromide (3.45 g., 0.043 mole) in glacial acetic acid (10 ml.). The mixture was heated on the steam-bath for 15 minutes, then left overnight at room temperature. The cooled solution deposited a solid which when recrystallized from benzene–petroleum ether (b.p. 60–68°) formed transparent, white needles (0.78 g.) melting at 154–155.5° dec. The analytical samples melted at 154–156° dec.

Anal. Calcd. for $C_{16}H_{13}NO_3Br_2$: C, 45.00; H, 3.07. Calcd. for $C_{16}H_{12}OBr_2$: C, 50.56; H, 3.18. Found: C, 49.01; H, 3.01; after recrystallized again, found: C, 49.38; H, 2.95.

This substance no longer contained the nitro group (ferrous hydroxide test) or nitrogen (sodium fusion followed by prussian blue test). It was unchanged by the action of bromine in carbon tetrachloride, potassium permanganate in acetone and potassium iodide in acetone. The substance could possibly be a bromocyclopropyl ketone.

Ic (2.13 g., 0.00616 mole) was added to glacial acetic acid (5 ml.) saturated with hydrogen bromide. The solid (unchanged Ic (84.5%)) was separated after 30 minutes.

2-Phenyl-5-*p*-bromophenylfuran (XVIII) from XIXa.—XIXa (1 g., 0.023 mole) was boiled overnight in alcohol (50 ml.) containing a little water (0.5 ml.). The yellow solution was concentrated and then cooled. The product XVIII (0.35 g., 50%), m.p. 121–125°, was removed and a second crop (0.17 g., 24%), m.p. 98–110°, was obtained from the filtrate. The nearly white analytical sample, re-

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(7) 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.

crystallized from alcohol and then sublimed, melted at 127–129°.

Anal. Calcd. for $C_{16}H_{11}OBr$: C, 64.23; H, 3.71. Found: C, 63.80, 63.99; H, 3.81, 3.55.

3-Nitro-2-phenyl-5-*p*-bromophenyl-2,3-dihydrofuran (XXI).—A suspension of XIXa (5 g., 0.0127 mole) and potassium acetate (5 g.) in absolute alcohol (30 ml.) was left at room temperature for two days. The tan solid was removed and recrystallized from benzene–petroleum ether (b.p. 60–68°). There resulted fluffy, white needles of XXI (0.72 g., 28%) melting at 165–168° dec. This substance reduced potassium permanganate in acetone. It was unchanged by the action of 2,4-dinitrophenylhydrazine under vigorous conditions such that even the least reactive stereoisomer of I formed a derivative. The ultraviolet absorption spectrum (2.67 × 10^{-5} *M* in U.S.P. 95% ethanol) showed a maximum at 267 mμ, ϵ 23,000. The analytical sample, recrystallized from absolute alcohol–benzene, melted at 167–168° dec.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 56.15; H, 3.42.

Thermal Decomposition of XXI to Form XVIII.—Only an impure red substance was obtained by heating XXI in alcohol with or without the addition of hydrochloric acid. When XXI (0.15 g., 0.00044 mole) was heated in a sublimation tube, initially at 170° and then for three days at 100–120°, XVIII (0.006 g., 5%), melting at 126.5–128°, sublimed away from the reddish-brown tar which formed the main product. The melting point of a mixture with authentic XVIII was undepressed.

Ozonolysis of XXI.—A solution of XXI (0.35 g., 0.001 mole) in ethyl acetate (140 ml.) was cooled in an ice-bath and ozonized oxygen (*ca.* 0.00015 mole O_3/min.) was passed through it until absorption of ozone ceased. Water (30 ml.) and acetic acid (6 ml.) were added and the mixture was boiled for 90 minutes; ethyl acetate was then removed by distillation. A low-melting yellow solid was present in the residual aqueous solution. The mixture was made alkaline by the addition of sodium bicarbonate, and the yellow solid (0.19 g.) was extracted into ether. An attempt to prepare a 2,4-dinitrophenylhydrazone from a portion of this substance was unsuccessful. The remainder of the neutral fraction decomposed before it could be identified.

Acidification of the aqueous bicarbonate solution caused the precipitation of a yellow acid (0.19 g., 95% as *p*-bromobenzoic acid), melting at 125–180°. This acid was sublimed. There could have been no more than a trace of benzoic acid present since it would sublime very readily, and the first traces of sublimate melted at 85–185°. The major portion of the product melted at 246–248° (sealed capillary). An authentic sample of *p*-bromobenzoic acid (melting point standard) melted at 245–247°. A mixture of the two melted at 246–248°.

The Action of Sodiomalonic Ester upon XXI.—To a suspension of XXI (1 g., 0.0029 mole) in absolute methanol (20 ml.), cooled in a Dry Ice–isopropyl alcohol bath, a solution of sodiomalonic ester (prepared from sodium (0.14 g., 0.006 mole), dimethyl malonate (0.79 g., 0.006 mole) and absolute methanol, (10 ml.)) was added. No change was apparent at this low temperature, at 0° or at room temperature. The mixture was boiled for three hours when it became red. It was then cooled and acidified (to *p*H 6) with acetic acid. A white solid (0.69 g., 69%), melting at 115–140° dec., was removed. After three recrystallizations from absolute methanol–benzene, XXI melted at 166.5–168.5° dec.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 56.40; H, 3.79.

Decomposition of XIXb in Boiling Alcohol.—A solution of XIXb (0.30 g., 0.0007 mole) in 95% alcohol (30 ml.) was boiled for six hours. The yellow solution was concentrated and cooled. Shiny white plates of XIXb (0.07 g., 23%) melting at 155–168° dec. separated. When recrystallized from alcohol, the substance melted at 170–173.5° dec. The melting point of a mixture with the starting material was undepressed.

A second crop of gummy yellow substance was obtained. After two recrystallizations from alcohol, the light yellow needles of XX (0.03 g., 12%) melted at 112–115.5°. The melting point of a mixture with the analytical sample of XX was not depressed. No XVIII could be isolated.

3-Nitro-4-phenyl-1-*p*-bromophenyl-3-buten-1-one (XX).—A suspension of XIXb (1.20 g., 0.0028 mole) and potassium acetate (1.2 g.) in absolute alcohol (10 ml.) was left overnight at room temperature. The solid was separated, washed with cold alcohol (3 ml.) then copiously with water, and dried. There resulted light yellow needles of XX (0.58 g., 60%) melting at 115–116.5°. The analytical sample, recrystallized from carbon tetrachloride–petroleum ether (b.p. 60–68°), melted at 117–118°.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 55.31; H, 3.74.

XX reduced potassium permanganate in acetone. The ultraviolet absorption spectrum (2.91 × 10^{-5} *M* in U.S.P. 95% ethanol) showed a maximum at 259 mμ, ϵ 24,600. There was a shoulder in the 300-mμ region. Extrapolation of the aroyl absorption through this region and subtraction of it left a broad maximum at 300–310 mμ, ϵ 7,500.

Ozonolysis of XX.—A solution of XX (0.50 g., 0.00145 mole) in ethyl acetate (100 ml.) was cooled in an ice-bath as a slight excess of ozonized oxygen was passed through (0.000151 mole O_3/min.); the solution was then swept out with oxygen. Water (30 ml.), acetic acid (6 ml.) and zinc dust (1 g.) were added, and the mixture was boiled for 1.75 hours to decompose the ozonide. The zinc was removed, most of the ethyl acetate was removed by distillation, and the residue was made alkaline by the addition of 5% aqueous sodium bicarbonate, and extracted with ether (three 50-ml. portions). The ether extract was washed with water, dried ($MgSO_4$) and evaporated. The residue partially solidified. A 2,4-dinitrophenylhydrazone melting at 235–237° was prepared from a portion of the residue. The melting point of a mixture with the same derivative of authentic *p*-bromoacetophenone was not depressed.

When the aqueous bicarbonate solution was acidified (dil. hydrochloric acid) no precipitate formed. The acidic solution was concentrated, and a small amount of white solid was removed, which melted at 124–235° with sublimation. This solid was sublimed. The first traces to sublime melted at 121–145° and the main portion melted at 245–247° in a sealed capillary tube. The melting point of a mixture with *p*-bromobenzoic acid was the same.

The distilled ethyl acetate gave a fuchsin test for an aldehyde. A 2,4-dinitrophenylhydrazone was prepared, but it was contaminated with the derivative of *p*-bromoacetophenone and could not be separated from it.

The Action of Sodiomalonic Ester upon XX.—XX (0.42 g., 0.0012 mole) was added to a solution of sodiomalonic ester (prepared from sodium (0.07 g., 0.003 mole), dimethyl malonate (0.40 g., 0.003 mole) and absolute methanol, (5 ml.)) and cooled in a Dry Ice–isopropyl alcohol bath. The immediate yellow coloration became red at 0°. After 15 hours at 0°, only a small amount of solid remained undissolved. The mixture was acidified with acetic acid, half of the solvent was evaporated in a current of air, and a fine, yellow crystalline substance (0.04 g.), melting at 129.5–131° dec., separated. When recrystallized twice from methanol, it melted at 140–141° (dec. at 148°). Only a tar was obtained from the filtrate.

Anal. Calcd. for $C_{21}H_{20}NO_7Br$: C, 52.95; H, 4.23. Calcd. for $C_{21}H_{19}O_5Br$: C, 58.48; H, 4.44. Found: C, 54.39; H, 4.07.

3-Nitro-2,4-dibromo-4-phenyl-1-*p*-bromophenyl-1-butanone (XXV).—Only unchanged Ic was isolated from experiments in which solutions of Ic and bromine in carbon tetrachloride were boiled under free radical conditions (ultraviolet and visible illumination and benzoyl peroxide).

Anhydrous hydrogen bromide was passed for three hours into a cooled (ice-bath) solution of a mixture of Ia and Ib (10 g., 0.029 mole) and bromine (5.0 g., 0.031 mole) in glacial acetic acid (500 ml.). The solution was left at room temperature for 17 hours, then poured into ice-water (2 kg.). The flocculent white solid was removed and dissolved in chloroform (150 ml.), and the solution was washed with water, then dried ($MgSO_4$) and concentrated. Petroleum ether (b.p. 60–68°) was added, and the solid (11.4 g.) was removed. Fractional crystallization from chloroform petroleum ether (b.p. 60–68°) gave pure XXVa (3.2 g., 22%), melting at 142–143° dec.

Anal. Calcd. for $C_{16}H_{12}NO_3Br_3$: C, 37.98; H, 2.39; Br, 47.38. Found: C, 37.95, 37.91; H, 2.58, 2.46; Br, 47.32, 47.45.

In a second experiment, a mixture of Ia and Ib (30 g., 0.087 mole) gave XXVa (11.3 g., 26.5%), melting at 142–143° dec., and XXVb (1.8 g., 4.1%), melting at 168–169° dec. The stereoisomers of XXV were separated by fractional crystallization from chloroform–petroleum ether (b.p. 60–68°). XXVb crystallized as white needles.

Anal. Calcd. for $C_{16}H_{12}NO_3Br_3$: C, 37.98; H, 2.39. Found: C, 37.96; H, 2.54.

In a third experiment, the bromination was incomplete. XIXa (16%) was isolated, and the presence of XXVa was indicated by the presence of the rhombic crystals although the substance was not isolated in a pure state.

In the fourth experiment, a mixture of Ia with Ib (30 g., 0.087 mole) gave XXVb (24.53 g., 56%) melting at 163–168° dec.

All experiments designed for the bromination of Ic were unsuccessful. The products were XIXb and unchanged Ic.

The Bromination of XIX.—A small amount of hydrogen bromide was passed into a solution of XIXa (10 g., 0.0234 mole) in glacial acetic acid (750 ml.). A small amount of bromine was added, and the solution was heated on the steam-bath until the color of the bromine faded. More bromine was added until the color of bromine persisted. The reaction mixture was processed in the usual manner to isolate XXVb (7.44 g., 63%), melting at 164–168° dec., and XXVa (0.70 g., 6%), melting at 142–143° dec.

Only unchanged XIXb (70%) was isolated from one attempt to brominate it. In another experiment, XIXb (0.40 g., 0.00094 mole) was converted into a substance (0.10 g.) melting at 129–132°. This substance did not give a ferrous hydroxide test for the nitro group and did not reduce potassium permanganate in acetone. It probably was formed by the displacement of the nitro group by a bromine atom.

Anal. Calcd. for $C_{16}H_{13}OBr_3$: C, 41.79; H, 2.85. Found: C, 41.88; H, 3.30

The Action of Potassium Iodide upon XXV.—It was quite difficult to isolate pure products from this reaction. In one experiment, XXVa (3.86 g., 0.0076 mole) and potassium iodide (4 g.) were suspended in ice-cold acetone (25 ml.). Iodine was liberated almost immediately. The mixture was kept at 0° for three days, then most of the acetone was evaporated in an air current, and aqueous sodium thiosulfate (50 ml., 0.54 *M*) and ether (100 ml.) were added. The ether layer was separated, washed with water, dried and evaporated. After some attempts to separate the products by crystallization, the residue (2.40 g.) was chromatographed from 1:1 benzene–petroleum ether (b.p. 60–68°) (35 ml.) on silica gel (65 g.) using benzene–petroleum ether (b.p. 60–68°) of gradually increasing benzene content (2:3, 1:1, 3:2 and 2:1) as eluting agent. Surprisingly, some of the iodine remained and came very rapidly through the column. The chief product (0.82 g., 31%) was XX, melting at 97–115.5°. After one recrystallization, it melted at 117.5–118° and did not depress the melting point of XX obtained by the action of potassium acetate upon XIXb. A sample of XX from XXVa was analyzed.

Anal. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49; Br, 23.09. Found: C, 55.78; H, 3.88; Br, 22.98, 23.32.

Among the other products of the reaction were a white solid melting at 242–244°, a white solid melting at 128–130° and, on one occasion, a light yellow solid melting at 95–97°. The analytical values of the 128°-substance suggested that it had the same composition as did the 1,3-diketone XIV. Since this substance could have been a 1,4-diketone, a fraction of the chromatogram melting at 121–127° was subjected to the action of concentrated sulfuric acid in the hope of converting it into the furan XVIII, but no XVIII was isolated.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C. 60.57; H, 4.13. Found: C, 60.47; H, 3.84.

The analytical values of the 95°-substance suggested that it might have had the same composition as did XX, differing from XX in location of the double bond. The ultraviolet absorption spectrum (3.00×10^{-5} *M* in U.S.P. 95% ethanol) showed one maximum at 259 mμ, ϵ 14,600, and another at 329 mμ, ϵ 17,600. Unfortunately, this substance was isolated but once in low yield. Careful examination of the chromatogram failed to disclose any of it (possibly the double bond is readily shifted to form XX). The small amount at hand was subjected to the action of sodiomalonic ester, but no pure product could be isolated from the reaction.

Anal. of 95°-substance. Calcd. for $C_{16}H_{12}NO_3Br$: C, 55.50; H, 3.49. Found: C, 55.90; H, 3.62.

The only product isolated from the action of potassium iodide (4 g.) upon XXVb (4.00 g., 0.0094 mole) was XX (0.22 g., 8%) melting at 117.5–118°. The identity of this product with the XX arising from XIXb was established by the melting point of a mixture of the two and by comparison of their ultraviolet spectra (maximum at 259 mμ, ϵ 24,600 and shoulder around 300 mμ).

Other Reactions of XXV.—No pure product could be isolated from the action upon XXV of alcoholic potassium acetate, methanolic sodiomalonic ester, or zinc dust in boiling alcohol.

3-Nitro-4-chloro-4-phenyl-1-*p*-bromophenyl-1-butanone (XXVII). From Ia.—Anhydrous hydrogen chloride was passed into a cooled (ice-bath) solution of Ia (3.00 g., 0.0087 mole) in glacial acetic acid (200 ml.) for four hours. The solution was left at room temperature for one day, then the product was isolated as was the hydrogen bromide adduct. The first crop was white needles of XXVII (1.05 g., 32%) melting at 130.5–133.5° dec. The analytical sample melted at 134–135° dec.

Anal. Calcd. for $C_{16}H_{13}NO_3BrCl$: C, 50.22; H. 3.42. Found: C, 50.44; H, 3.66.

The second crop was fluffy white needles of the 1:1 complex of XXVII with XXVIIIb (1.60 g., 51%) melting at 111–112°. The analytical sample also melted at 111–112°. It slowly reduced potassium permanganate in acetone.

Anal. Calcd. for $C_{32}H_{25}NO_4Br_2Cl_2$: C, 53.50; H, 3.51. Found: C, 53.79; H, 3.78.

From Ib.—A similar experiment was performed with Ib (2.00 g., 0.0058 mole). The first crop consisted of XXVII (0.24 g., 11%) melting at 131.5–134° dec. The melting point of a mixture with the analytical sample was not depressed. The second crop, after recrystallization from benzene–petroleum ether (b.p. 60–68°), yielded Ic (0.24 g., 12%) melting at 163–164°. The melting point of a mixture with authentic Ic was undepressed. The third and fourth crops were recrystallized from the same solvent to obtain impure XXVII (0.18 g., 8%) melting at 129.5–132° dec.

Only unchanged Ic (84%) was isolated from the action upon Ic of hydrogen chloride in absolute alcohol or in acetic acid, at 0°, room temperature or 80°.

Conversion of XXVII into the Furan XVIII.—A solution of XXVII (0.25 g., 0.00065 mole) in alcohol (50 ml.) and water (one drop) was boiled for 16 hours. The solution was then concentrated (4 ml.) and cooled. Fine, white needles of XVII (0.06 g., 30%), melting at 125.5–127.5°, separated. The melting point of a mixture with authentic XVII was undepressed. The second crop (0.03 g., 15%) melted at 98–122°.

The 4-Chloro-4-phenyl-1-*p*-bromophenyl-3-buten-1-one (XXVIII).—A suspension of XXVII (0.75 g., 0.0020 mole) and potassium acetate (0.75 g.) in absolute alcohol (20 ml.) was left at room temperature for two days. The solid was removed and recrystallized from alcohol–benzene, when it formed downy white needles of XXVIIIa (0.08 g., 12%) melting at 180–182°. The analytical sample, crystallized from alcohol–benzene, melted at 182.5–184°.

Anal. Calcd. for $C_{16}H_{12}OBrCl$: C, 57.26; H, 3.61. Found: C, 60.23; H, 4.13.

Another analytical sample, melting at 183–184°, was crystallized from benzene–petroleum ether (b.p. 60–68°). The ultraviolet absorption spectrum of this substance (2.78×10^{-5} *M* in U.S.P. 95% ethanol) showed a maximum at 265 mμ, ϵ 22,500. The substance readily reduced potassium permanganate in acetone, and gave no precipitate by the action of alcoholic silver nitrate.

Anal. Calcd. for $C_{16}H_{12}OBrCl$: C, 57.26; H, 3.61. Found: C, 59.90; H, 3.53.

A small amount of flocculent crystals of a second substance, melting at 124–124.5°, was isolated. Attempted sublimation gave a liquid which solidified on standing. The solid melted at 130–132°. A mixture with XXVIIIb obtained from the complex melted at 130–133°.

XXVIIIb from the 111°-Complex.—A suspension of the complex of XXVII and XXVIIIb (1.40 g., 0.00196 mole) and potassium acetate (1.4 g.) in absolute alcohol (10 ml.) was boiled for ten minutes, then left at room temperature for 90 minutes. A yellow solid (0.72 g.), melting at 105–114° separated; light yellow needles of XXVIIIb (0.52 g., 40%), melting at 131.5–132.5°, were obtained by recrystallization from benzene–petroleum ether (b.p. 60–68°). The analytical sample, obtained by further recrystallization from the same solvent, melted at 132.5–133°. It slowly reduced potassium permanganate in acetone, and gave no test for reactive halogen with alcoholic silver nitrate.

Anal. Calcd. for $C_{16}H_{12}OBrCl$; C, 57.26; H, 3.61. Found: C, 57.35; H, 3.56.

MINNEAPOLIS, MINNESOTA

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

Cyclopropanes. XVIII. 1-*p*-Bromobenzoyl-2-nitro-3-phenylcyclopropane: Configurations of the Stereoisomers[1]

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

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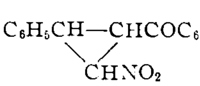
On the basis of chemical studies described in the preceding two papers, it has been possible to deduce the configurations of the three known stereoisomers of the cyclopropane I named in the title. The arguments lead to configuration F for isomer Ia, to configuration E for isomer Ib, and to configuration D for isomer Ic.

A cyclopropane of structure I may exist in four racemic forms. Three of these four stereoisomers have been obtained, as described in the two previous papers. These are Ia, melting at 135.5–136°, Ib, melting at 120.5–121°, and Ic, melting at 166.5–167.5°.



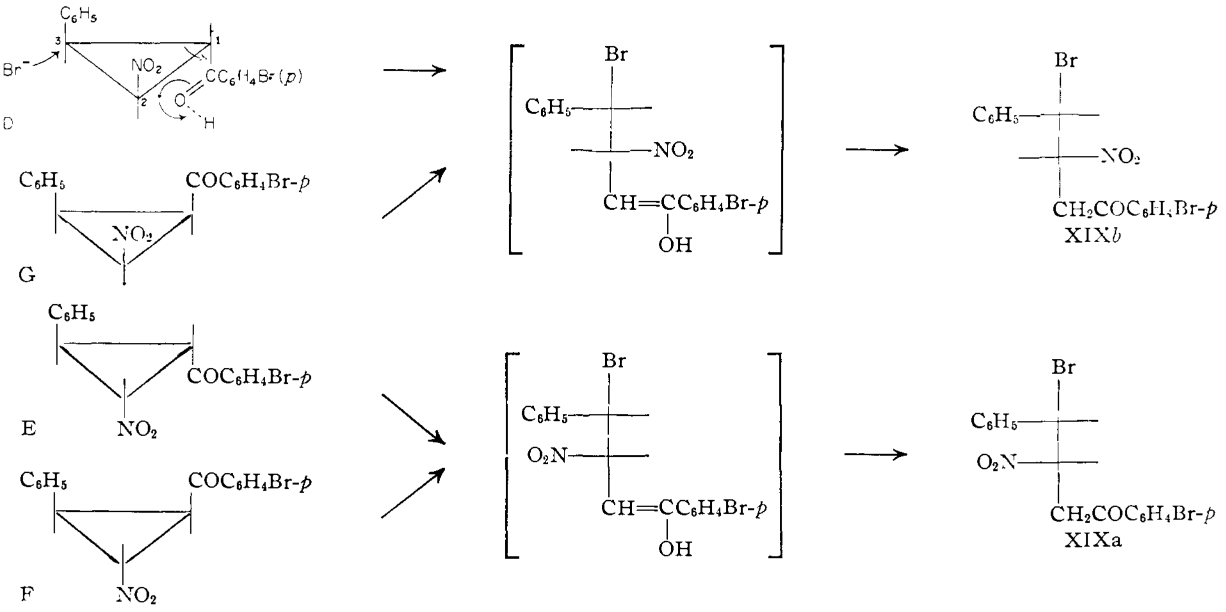
$$C_6H_5CH{-}CHCOC_6H_4Br\text{-}p \quad (\text{ring closed by } CHNO_2)$$

I

It has been possible to make some deductions concerning the configurations of these stereoisomers based upon the results described in the two previous papers. The relevant facts are these:

1. Ia and Ib, by action of hydrogen bromide, are converted into the same adduct XIXa, whereas Ic is converted into a stereoisomeric adduct XIXb.[3] 2. Ia and Ib, by action of hydrogen chloride, are converted into the same adduct XXVII, whereas Ic is unaffected by this reagent. 3. The respective rates at which the cyclopropyl ketones are converted into 2,4-dinitrophenylhydrazones vary quite widely and are in the order Ic > Ib > Ia. 4. The nitrodihydrofuran XXI is recovered unchanged after action of methanolic sodiomalonic ester. 5. Action of mild bases results in conversion of Ia into Ib and Ic; of Ib into Ic; and has no effect upon Ic.

The four racemic forms of I may be represented by D, E, F and G. Facts 1 and 2 above indicate that the reaction between I and hydrogen halide is stereospecific and, consequently, a concerted process. If this were not true, each stereoisomer of I would have been converted into either the more stable stereoisomer of XIX (and of XXVII) or else a mixture of the stereoisomers of XIX (and of XXVII) would have been produced. The mechanism of the addition reaction, therefore, must have consisted of an attack by bromide ion at the back of C-3 as a proton attacked the oxygen



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(1) Paper XVII, THIS JOURNAL, 78, 1475 (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) The numbering of the compounds cited in this paper is the same as that in the two previous papers, so that the numbers refer to the same compounds in all three papers.