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]

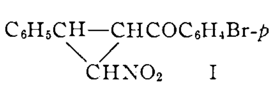
# Cyclopropanes. XVIII. 1-*p*-Bromobenzoyl-2-nitro-3-phenylcyclopropane: Configurations of the Stereoisomers[1]

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

RECEIVED SEPTEMBER 23, 1955

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°.



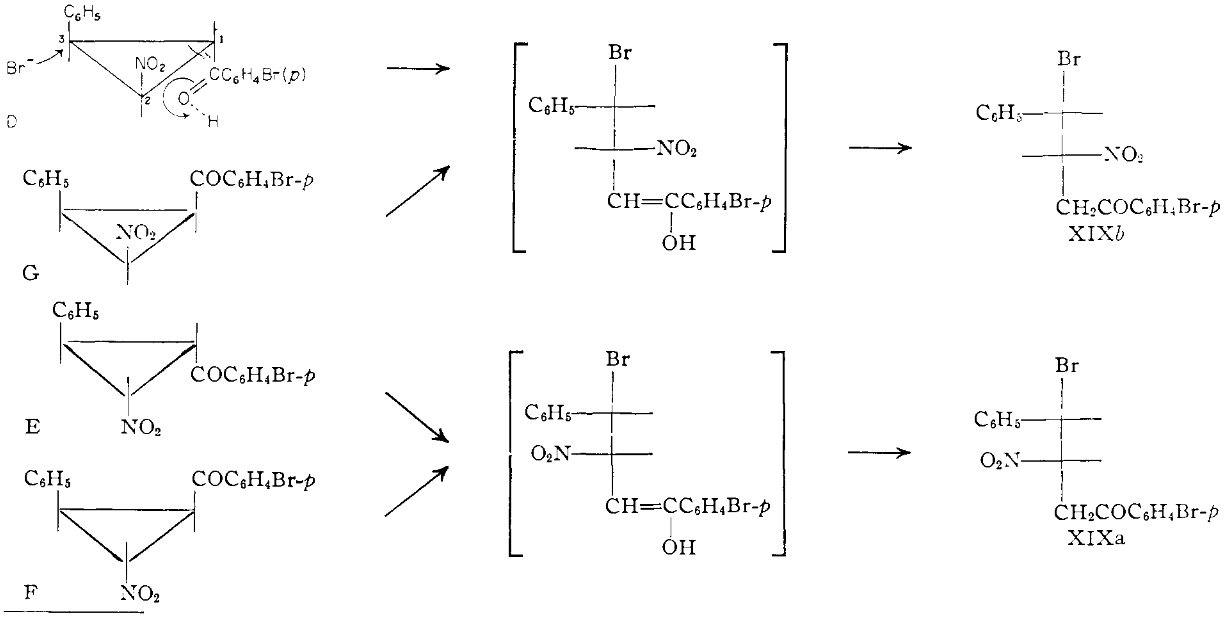
$$C_6H_5CH—CHCOC_6H_4Br\text{-}p \quad (\text{bridged by } CHNO_2)$$

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



---

[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.

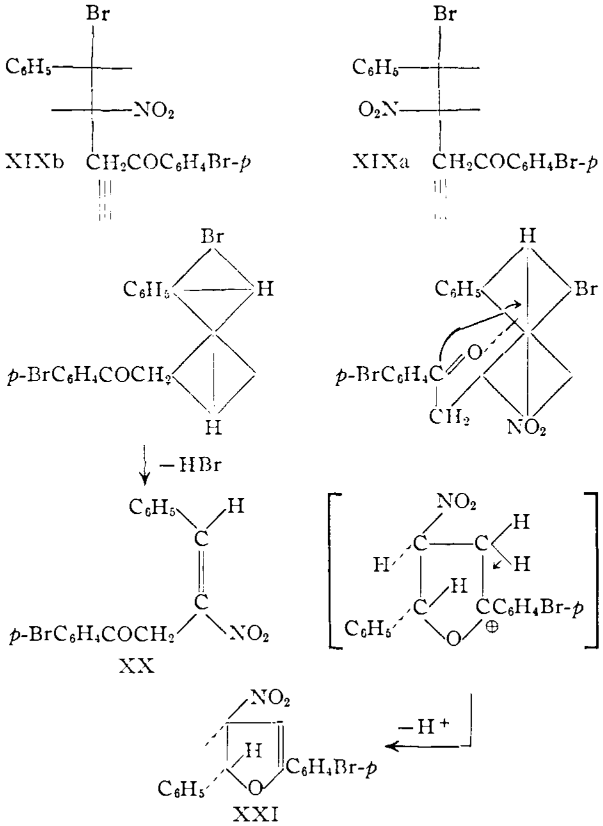
[3] The numbering of the compounds cited in this paper is the same as that in the two previous papers, so that the numbers refer to the same compounds in all three papers.

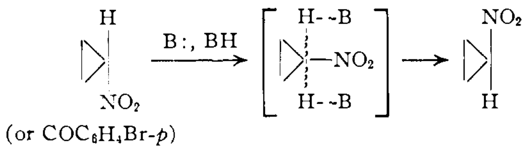
atom of the carbonyl group, weakening the bond between C-1 and C-3. The configuration at C-3 is thus inverted, the configuration at C-2 is unchanged, and C-1 lost its asymmetry. Ia and Ib, therefore, differ in configuration only at C-1 since they produced the same adducts. Ic then, differs from Ia and Ib in the relative configurations at C-2 and C-3. Hence Ia and Ib have configurations D and G, or else E and F, and Ic is one of the remaining pair. Fact 3 shows that Ic possesses the most active carbonyl group, Ia the least reactive carbonyl group, whereas the carbonyl group of Ib lies between these two in reactivity toward 2,4-dinitrophenylhydrazine. Consequently, Ic is not G, the isomer with the most hindered carbonyl group, and Ia and Ib are not D and G, with, respectively, the least hindered and the most hindered carbonyl groups. Therefore Ia and Ib are E and F, and Ic is D. Also XIXa and XIXb have the configurations shown.

It follows further that, by a *trans*-1,2-elimination of the elements of hydrogen bromide from XIXb, XX would be formed as the stereoisomer having the phenyl group *trans* to the nitro group, whereas formation of XXI *via* a displacement of bromide ion by the oxygen atom of the carbonyl group of XIXa would lead to that stereoisomer of XXI having the phenyl group *trans* to the nitro group. These should be the more stable stereoisomers of XX and of XXI. Fact 4—that XXI is unaffected by action of sodiomalonic ester—supports the assignment of the *trans* configuration to XXI, for this reagent would be expected to remove the hydrogen atom in the $\alpha$-position to the nitro group, destroying the asymmetry at C-3. Return of the hydrogen atom, on subsequent acidification, should lead to formation of the stable *trans* form of XXI. Thus the configurations assigned to the precursors of XXI are also supported.

Fact 5 shows that Ic is the most stable of the stereoisomers, whereas Ia is the least stable. Piehl and Brown[4] have expressed the opinion that interconversion of cyclopropanes must involve the reversible removal of a proton to form an open-chained anion. Aside from the question as to why such an anion should revert to a cyclopropane instead of being converted into an isomer thereof such as XX, XXI or XXVI, or into one of the products formed by action of strong bases such as XIV or XV, there remains the fact that the anion would have lost the asymmetry of the cyclopropane and should revert to the most stable isomer Ic, and this process would not account for the transformation of Ia into Ib.

It seems more reasonable, rather, that the ring is not opened and that the process involves an acid-base catalyzed inversion of configuration at C-1 or C-2 wherein the substituent is in the plane of the ring in the transition state, and that the greater stability of the final configuration supplies the driving force for the conversion.





If such a mechanism is valid, E and F (Ia and Ib) could be interconverted by an inversion at C-1. E could be converted into D (Ic) by an inversion at C-2. F could be converted into D *via* three routes: an inversion at C-1 to give E followed by an inversion at C-2; an inversion at C-2 to give G followed by an inversion at C-1; or an inversion at C-3. The second route may be rejected because it involves the unknown, highly hindered configuration G. The third route requires reaction at C-3 where the least acidic hydrogen atom is located. It follows, therefore, that the first route is the most probable one, and if this be so, Ia should have configuration F and Ib should have configuration E. Ib was more strongly adsorbed on silica gel than was Ia which supports the assignment of the *cis* orientation of the polar groups (configuration E) to Ib and the *trans* orientation to Ia.

MINNEAPOLIS 14, MINNESOTA

---

[4] F. J. Piehl and W. G. Brown, THIS JOURNAL, **75**, 5023 (1953).