C.—*Properties of Conjugated Compounds. Part IV. The Formation of Isomeric Additive Dibromides from Butadiene.*

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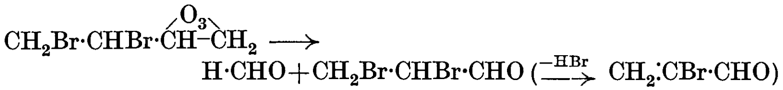
Certain conjugated hydrocarbons have been found to yield additive dibromides and hydrobromides of two types, representing attachment of the addendum at adjacent and at terminal carbon atoms of the chain, respectively. This fact would seem to constitute direct evidence in favour of that attractive extension of the Thiele hypothesis which has been developed in connexion with electronic theories of polarisation. It is held that the butadienoid unit may polarise in two ways, $\mathrm{C{-}C{-}\overset{+}{C}{-}\overset{-}{C}}$ and $\mathrm{\overset{+}{C}{-}C{-}C{-}\overset{-}{C}}$, leading to reaction at adjacent (1 : 2- or 3 : 4-) or terminal carbon atoms of the chain. On this basis terminal addition is no longer *required*, but may be explained when it arises during the course of experiment. With precisely those conjugated compounds, however, from which two isomeric additive products have been isolated, there is evidence to show that one additive form is readily convertible into the other. The question therefore arises whether both are primary products of addition.

The addition of bromine to butadiene was examined by Griner (*Compt. rend.*, 1893, **116**, 723; **117**, 553). This author records the formation (in chloroform solution at −21°) of only one dibromide. This substance, a liquid, changed slowly in the cold and rapidly at 100° into a solid isomeride, m. p. 53—54°. The liquid and the solid were respectively considered to be the 1 : 2- and the *trans*-1 : 4-dibromide of butadiene. Conversion of the liquid form into the solid, by heating, was not complete : a small amount of liquid dibromide remained which, although almost undifferentiated in boiling point from the original liquid form, was considered to be the *cis*-1 : 4-dibromide. The accuracy of these observations was contested by Thiele (*Annalen*, 1899, **308**, 333), who stated that under essentially the conditions of Griner the predominant product of bromine addition was the solid, m. p. 53—54°. The constitution of a small liquid residue was left undetermined. Since the 1 : 4-position of the bromine atoms in the solid compound followed readily from its oxidation product, butadiene was regarded as yielding mainly—probably exclusively—a terminal dibromide. Although the additive formation of both 1 : 4- and 1 : 2-dibromides has more recently been admitted by Thiele (Straus, *Ber.*, 1909, **42**, 2872), there is, as far as we are aware, no record in the literature of a repetition of the experiment.

Under the conditions described by both Griner and Thiele, butadiene invariably unites additively with bromine to yield a mixture of two dibromides. One of these, a liquid which corresponds to Griner's product in boiling point and instability, is the 1 : 2-dibromide, since its ozonide on fission gives excellent yields of αβ-dibromopropaldehyde and formaldehyde; the other is the solid compound described by Griner and Thiele and shown by the latter to possess the 1 : 4-constitution.



$$CH_2Br\cdot CHBr\cdot \overset{O_3}{CH{-}CH_2} \longrightarrow H\cdot CHO + CH_2Br\cdot CHBr\cdot CHO\ (\xrightarrow{-HBr} CH_2{:}CBr\cdot CHO)$$

When *either* the 1 : 2- or the 1 : 4-dibromide is heated for a few minutes at 100°, the product is a mixture in which the two isomerides appear to be in equilibrium $[1:2 \rightarrow 1:2\ (20\%) + 1:4\ (80\%) \leftarrow 1:4]$. The 1 : 2-constitution of the liquid portion of the mixture, whether derived by the forward or by the backward change, has been established by ozonisation. No indication of the formation of a third isomeride (the *cis*-1 : 4-dibromide of Griner) has been obtained;* if, however, the heating be prolonged for several hours, a new liquid of considerably higher boiling point, probably a polymeride, makes its appearance. At room temperature the change 1 : 2- ⟶ 1 : 4- takes place slowly and approaches completion in about four days if crystallisation of the solid form be promoted; if crystallisation is not assisted, the system tends apparently to a metastable condition. At room temperature the reverse change is inappreciable. Both dibromides readily liberate iodine from potassium iodide dissolved in acetic acid. The liberation is most rapid with the 1 : 2-dibromide, but quantitative measurements are rendered difficult owing to the recombination of the liberated iodine with the bromohydrocarbon. Figures approaching one molecule of liberated iodine per molecule of dibromide have been obtained.

In a series of theoretical papers (*Bull. Soc. chim. Belg.*, 1921—1922) Gillet has reviewed many known cases of intramolecular change among unsaturated compounds. These involve migration of an atom or radical (OH, Br, H) with accompanying double-bond movement. He submits the generalisation : "If in the system $C_1{:}C_2{\cdot}C_3X$ the total effect of the radicals saturating C_3 is strongly negative in comparison with that of the groups saturating C_1, the most negative radical attached to C_3 tends to migrate to C_1" (*ibid.*, 1922, **31**, 365). The additive dibromides and dihydrogenated derivatives of conjugated compounds would be expected to exemplify this rule, and of the former Gillet says : "If one compares the compound $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2Br$ with the examples cited (examples which follow the rule) it is found to be in the same category and should very easily undergo, under the influence of traces of acid, the transformation $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2Br \longrightarrow CH_2Br{\cdot}CH{:}CH{\cdot}CH_2Br$. Thus in effect two forms are obtained by combining one molecule of bromine with one molecule of butadiene, the second form preponderating." Addition is therefore regarded as taking place at one double bond, the apparent 1 : 4-addition being sufficiently explained by including the 1 : 2-dibromide in the category of substances subject to "negative" migration.

During the course of our experiments Prévost has published observations (*Compt. rend.*, 1927, **184**, 1460) concerning the addition of bromine to ααδδ-tetramethylbutadiene. Here the dibromide

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* Owing to the mobility of the liquid dibromide and the ready solubility of the solid dibromide in its liquid isomeride (also the volatility of the former in the vapour of the latter) it is particularly difficult to demonstrate conclusively, as, *e.g.*, by oxidation or distillation methods, the absence of a *cis*-1 : 4-isomeride. This point is being closely examined in the less mobile bromo-compounds derived from certain substituted butadienes.

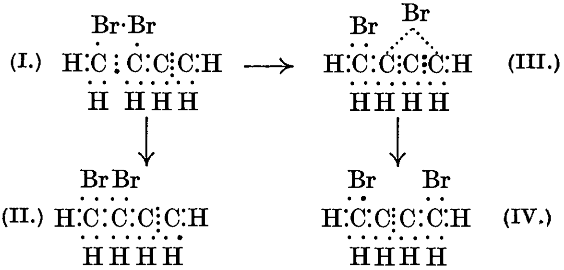
consists of a mixture of solid (10—20%) and liquid material when first isolated, but the liquid portion solidifies so rapidly, and decomposes so readily on distillation, that a definite liquid dibromide isomeric with the solid compound cannot be separated. The solid is regarded as the 1 : 4-form, and the liquid as a solution of this form in its 1 : 2-isomeride. From indications afforded by the variation of the melting point of the solid form with rapidity of heating and of the rapidity of solidification of the fused mass with duration of heating, it is concluded that the behaviour of the isomerides conforms with a principle of tautomeric interchange similar to that laid down by Gillet, but reversible. The re-statement of Lapworth's $\alpha\gamma$-rule on a basis of ionisation (" synionism ") by this author (*ibid.*, 1927, **185**, 132) is of interest in that it identifies the activated form of the system $A{:}B{\cdot}CX$ with the ionised form $A\pm B\mp C\pm,X\mp$, employing the nomenclature of alternate polarity. The inclusion of additive dibromides of butadienoid hydrocarbons among mobile propene systems has, however, only an indirect bearing on the additive mode of the conjugated hydrocarbons unless (1) the primary additive dibromide is invariably a 1 : 2-compound, or (2) the tautomeric complex, $CH_2Br{\cdot}\underset{\cdot}{C}H{\cdot}CH{:}CH_2$, is in some form a necessary feature of the additive mechanism. If the sole primary additive dibromide of butadiene is the 1 : 2-compound, then the proportion of the two isomerides in the crude bromination mixture might be expected to vary with those conditions which affect the 1 : 2- → 1 : 4-change. Actually, although the proportion of isomerides obtained during bromination shows great constancy under given experimental conditions, it varies widely with the solvent employed. The table shows the percentage of 1 : 4-dibromide obtained in the presence of four carefully purified solvents, pure bromine being employed.

Chloroform	(−15°), 63·0.	Acetic acid	(4°), 70·0.
Hexane	(−15°), 38·4.	Carbon disulphide	(−15°), 65·9.

The rate at which the pure 1 : 2-dibromide isomerises in solvents such as hexane and chloroform, at temperatures below 20°, is variable but very slow. Change which occurs subsequently to the formation of the 1 : 2-dibromide and in which only the latter compound and the solvent participate, appears, therefore, an insufficient explanation of the considerable percentages of 1 : 4-dibromide recorded. The employment of slightly impure (commercial) instead of pure solvents during the bromination process caused little variation from the figures given above. Hydrogen bromide suggests itself as a probable accelerator of the 1 : 2- ⟶ 1 : 4-change, particularly as it is produced (apparently inevitably) during the bromination of butadiene. This reagent does undoubtedly accelerate the change in solution, but the extent of acceleration (see p. 738) falls far short of that which would be required for the formation of 38—70% of 1 : 4-dibromide during the time occupied by, and at the temperature of, bromination. Attempts to decrease the concentration of hydrogen bromide during bromination by suspending or dissolving appropriate reagents in the solvent led only to comparatively small reductions in the proportions of 1 : 4-dibromide (p. 737).

Although in a newly formed, extremely mobile system, the product isolated could be other than that first formed, in the present instance the degree of mobility appears insufficient to account for a considerable degree of 1:2 ⟶ 1:4-change within the required limits of time and temperature, unless acceleration is to be attributed to energy changes associated with a progressing reaction. It appears from this result that isomeric change of a purely post-additive nature is not to be regarded as mainly responsible for the appearance of two kinds of additive product. It remains, therefore, either to attribute the constitutional differentiation of the products to an inherent capacity of the hydrocarbon for assuming differently polarised forms, or to regard it as in large measure incidental to the operation of the additive mechanism. Of these alternatives, only the latter needs consideration, one of the principal objects of the present series of investigations being to examine the possibility of accounting for the additive products of so-called conjugated compounds without having recourse to a special hypothesis of conjugation.

It is clear that if reversible $\alpha\gamma$-change of the type $\cdot CBr\cdot C\colon C \rightleftharpoons C\colon C\cdot CBr$ (considered as purely of an intimate intramolecular character—that is to say, not proceeding by effective ionisation of bromine) is comparatively slow when the substances in question are the formed molecules of 1 : 2- and 1 : 4-dibromide, it is necessary to look to an earlier stage in the additive process for the chief cause of the differential orientation of the additive products. Thus, there is every appearance of the possession by an *intermediately* formed molecule or additive complex of a mobility superior to that of the corresponding formed molecules (compare "the enhanced mobility of *newly formed* molecules," Ingold and Goss, J., 1925, **127**, 2776). If, then, the additive reactions of butadienes are fundamentally of normal ethylenic character, the first additive stage of butadiene should be identical with that of ethylene under analogous conditions. Since in non-ionising solvents at any rate, there is strong probability of molecular attack by bromine (compare Soper and Smith, J., 1926, 1582; 1927, 2757) the intermediate compound may be represented (electronically) by a formula such as (I), although, possibly, attachment of the addendum at the two carbon atoms is achieved successively rather than simultaneously.



This has only transient existence, and breaking of the singlet linkage between the bromine atoms allows activity in two ways : (*a*) taking the course normal in the bromination of ethylenes, yielding (II), (*b*) bringing into action the tautomeric capacity of the propene system and passing through (III) to (IV). In this way conditions tending to the initiation of the $\alpha\gamma$-change (an absence of that fixity appertaining to the formed molecules which restrains the progress of the 1 : 2- ⇌ 1 : 4-change) occur in the normal course of addition, and activity of the propene system, in the sense indicated, is rendered the more probable by knowledge of propenoid behaviour derived from other sources. There is, of course, nothing in the evidence now submitted which definitely excludes the possibility of the formation of two intermediate complexes (corresponding to alternative polarisations of the hydrocarbon) in the additive process, but the observations recorded indicate a method of diminishing the probability in this direction by demonstrating the adequacy of propenoid activity to account for the differentiation of additive products.

Experiments with the additive dibromides of other butadienoid hydrocarbons have shown that reversible interconversion of 1 : 2- and 1 : 4-forms takes place either spontaneously or on heating (unless heating causes degradation). Little is known as yet concerning the equilibration of these compounds in solution or the correspondence (in composition) of equilibrium mixtures obtained under different conditions. Therefore, it is not possible to gauge the degree of approach to a condition of equilibrium between 1 : 2- and 1 : 4-forms attained in the bromination process. Doubtless, however, modification of the butadiene system by the introduction of substituents will have an effect on the composition of original bromination products generally analogous to that of substituents in aromatic processes and approximating towards that exerted in the 1 : 2- → 1 : 4-change in the sense foreseen by Gillet. Experiments in this direction are now being made, employing variously substituted butadienes and addenda of different types.

EXPERIMENTAL.

$\Delta^{\alpha\gamma}$-Butadiene was readily obtained from the gas which is liberated on heating "railway hydrocarbon"; this was passed into bromine until decolorisation was complete. The product became semi-solid on cooling owing to separation of butadiene tetrabromide. The latter compound was filtered off, washed with ligroin, and twice recrystallised from the same solvent (m. p. 117°; compare Thiele, *loc. cit.*). The filtrate contained a quantity of the stereoisomeric tetrabromide (m. p. 37—39°), but since this was difficult to purify in comparison with the higher-melting compound, the former was used exclusively for regenerating butadiene. The method of Thiele (*loc. cit.*) was employed for regeneration, the tetrabromide being placed in a percolator, from which condensed alcohol from the reaction flask gradually removed it. The issuing gas, after passing through efficient water-cooled condensers, was scrubbed by passage through U-tubes packed with calcium chloride and maintained at 0°. The gas was directly absorbed by solvent maintained at a low temperature, the quantity absorbed being estimated from the increase in weight. Owing to the ease with which butadiene is lost from many solvents, a content figure considerably lower than that indicated by weighing was assumed in the following bromination experiments. The yield, when the gas was absorbed in chloroform, was usually about 80%.

Method of Bromination.—A solution of the hydrocarbon in the desired solvent was prepared in a flask closed by a stopper carrying the delivery tube and a calcium chloride tube. After the weight of dissolved hydrocarbon had been ascertained, the stopper was rapidly exchanged for one carrying a small dropping-funnel and a calcium chloride tube. The required quantity of bromine was introduced into the dropping-funnel, which was then closed by a calcium chloride tube. The flask was cooled in a freezing mixture of ice and salt and the contents thereof were kept in thorough agitation during the entire period of bromination (about 1 hour for 5 g. of hydrocarbon). On opening the flask, fumes of hydrogen bromide usually escaped. The solvent, except in the case of acetic acid, was evaporated at greatly reduced pressure without heat-application. In those experiments in which glacial acetic acid was employed the bromination mixture was divided into two equal portions, which were worked up in different ways, and the results were compared. From one portion the solvent was removed at greatly reduced pressure, the containing flask being immersed in a beaker of water at 25°, whereas from the other it was removed by pouring the mixture into water, extracting the dibromide with ether, and repeatedly washing the ethereal solution with water. The subsequent removal of ether from the dried solution was conducted at reduced pressure. The total yield of dibromide and the proportion of solid dibromide were found to be nearly identical for each method.

Purification of the reagents was effected as follows: Bromine: (1) method of West, J., 1924, **125**, 1279; (2) a process essentially the method 3 of Orton, Watson, and Hughes (J., 1927, 2462). Acetic acid: method of Backes, West, and Whiteley (J., 1921, **119**, 364). Chloroform: washing with water, followed by agitation with concentrated sulphuric acid and final distillation over phosphoric oxide. Carbon disulphide: shaking with metallic mercury, followed by distillation over phosphoric oxide. Hexane: sodium-dried *n*-hexane of commerce (b. p. 68—69°) first carefully fractionated under an efficient column, then refluxed for 6 hours over sodium wire, and finally distilled. Quinoline dibromide hydrobromide was recrystallised twice from alcohol [Found: Br, 64·2 (total); 42·5 (available). Calc.: Br, 64·8 (total); 43·2 (available)%].

Separation of Dibromides.—The mixture of dibromides was diluted with an equal volume of petroleum (b. p. 40—60°) and cooled gradually (to obtain compact crystals) to −20°. After remaining at this temperature for 1 hour, the mother-liquor was decanted from the crystals, which were rapidly washed by decantation with a further very small amount of petroleum, the washings being added to the mother-liquor. The process was twice repeated. The liquid dibromide was isolated from the ultimate mother-liquor by evaporation of the solvent at reduced pressure. In the earlier experiments the halogen content of the crude liquid was determined; in each case so determined, the value found corresponded very closely with the required figure and the estimation was subsequently dispensed with. Owing to slight loss by volatilisation during the removal of the solvent, the total yield of dibromide in each experiment was slightly in deficit (usually about $1\frac{1}{2}$%) of the theoretical quantity calculated on the basis of the bromine employed.

The solid dibromide, $\alpha\beta$-dibromo-Δ^{β}-butene, crystallised in colourless prisms, m. p. 53° (Found: Br, 74·8. Calc.: Br, 74·8%). The intensely lachrymatory nature of this substance rendered it very objectionable to work with. The liquid dibromide was a colourless, mobile oil, which distilled without degradation (b. p. 58—66°/14 mm.), but suffered in the process a considerable degree of conversion into its solid isomeride (Found: Br, 74·7%).

Constitution of the Liquid Dibromide.—A solution of purified dibromide (6·5 g.) in chloroform was cooled in a freezing mixture whilst submitted to a current of ozonised oxygen (8 hours). The solvent was removed at reduced pressure, and the colourless, viscous ozonide decomposed by warming it gently with water. The formaldehyde, which was fully evolved during the decomposition, was absorbed in dilute ammonia and subsequently recovered as hexamethylenetetramine. The aqueous liquor, which contained much oil in suspension, was extracted with ether, the extract being shaken with a little sodium bicarbonate solution and finally dried. Distillation of the solvent (the distillate containing formaldehyde) left a pale yellow aldehydic oil, rich in bromine. This substance, αβ-dibromopropaldehyde, was converted for convenience into α-bromoacraldehyde by heating on a steam-bath for 20 minutes with aqueous sodium acetate (10 g. in 10 c.c.). The resulting liquor yielded on steam distillation a pale yellow, lachrymatory oil, b. p. 55°/17 mm. (Found: C, 26·7; H, 2·0; Br, 59·4. Calc.: C, 26·7; H, 2·25; Br, 59·25%), which was strongly aldehydic, yielding a semicarbazone, m. p. 160°, identical with that of α-bromoacraldehyde prepared by the method of Auwers and Heyna (*Annalen*, 1923, **434**, 140). The yields were excellent.

Composition of the Bromination Mixture.—The percentages of the 1 : 4-dibromide obtained in the different experiments are shown in the table. The figures are calculated on the ratio of 1 : 4-dibromide to the total dibromide isolated; the figures in brackets are the corresponding values based on the amount of bromine employed. The solvents and brominating agent were carefully purified, except where indicated as ordinary commercial reagents (com.).

Solvent.	Brominating agent.	Added reagent.	1 : 4-Dibromide %.
Chloroform.	Bromine.	—	63·0 (62·5)
"	Quinoline dibromide hydrobromide.	—	0
Chloroform (com.).	Bromine (com.).	—	63·7 (62·1)
Hexane.	Bromine.	—	38·4 (36·5)
"	"	Quicklime.	36·3 (35·2)
"	"	Calcium carbonate.	36·9
Acetic acid.	"	Potassium acetate.	69·2 (66·3)
Acetic acid (com.).	Bromine (com.).	—	70·3 (67·6)
Carbon disulphide.	Bromine.	—	65·9 (64·0)

Interconversion of the Butadiene Dibromides.—The liquid dibromide isomerises slowly even at room temperature. The change became appreciable in 3—4 days as indicated by diluting a specimen with petroleum and cooling to −15°; the introduction at this stage of a large crystal of the solid dibromide usually led to almost complete conversion into the solid isomeride in the course of a few days, but specimens left undisturbed remained liquid after standing for several weeks. At higher temperatures isomerisation was more rapid and at 100° conversion to the extent of about 80% could be effected in a few minutes. The solid form, stable at room temperature, likewise suffered isomerisation at higher temperatures. The identity of the liquid bromide so produced with the 1 : 2-dibromide derived directly from butadiene followed from its boiling point, its re-convertibility into the 1 : 4-dibromide, and the formation of formaldehyde and α-bromoacraldehyde on decomposition of its ozonide: there was no indication of a third isomeride, the *cis*-1 : 4-dibromobutene of Griner. The effect of heating the 1 : 4-dibromide at 100° over periods varying from 10 minutes to 3 hours was in all cases to produce a mixture of 1 : 2- and 1 : 4-isomerides. There was every appearance that at 100° equilibrium between the two forms became very rapidly established, since the composition of the mixtures produced by heating for periods up to ¾ hour varied little (solid 80%, liquid 20%); gradually, however, owing to slight degradation and the accumulation of a by-product of high boiling point (probably polymeric), the composition became changed and after 3 hours only 68% of the mixture consisted of the solid isomeride.

A knowledge of the facility of isomerisation of the liquid dibromide when dissolved in solvents such as chloroform and maintained under temperature conditions similar to those employed during bromination was a matter of importance. Specimens of the pure liquid dibromide, dissolved in hexane or chloroform at −15° and maintained for appropriate periods at this temperature, were found on examination (by the method utilised in separating the products of bromination) to have suffered only slight change, amounting to not more than a few units %. The change under similar conditions with acetic acid was rather greater but still small. The introduction of small quantities of hydrogen bromide into solutions of the pure liquid dibromide appeared to have in every case a definite accelerating effect, but this was not marked, amounting, for example, with chloroform only to 8% conversion. In no instance was a considerable conversion in solution effected at a low temperature and even at room temperature the degree of conversion became important only after a prolonged period.

Lability of Bromine in Butadiene Dibromides.—Both 1 : 2- and 1 : 4-dibromides liberated iodine from a glacial acetic acid solution of potassium iodide at room temperature. With the former the initial speed of liberation was the greater, but after a time the progress of the reaction could not be followed owing to the combination of iodine with the unsaturated compounds in solution. At 40° the combination of liberated iodine was still more marked. No really satisfactory method of estimation was discovered, although by periodic titration of the reaction mixture with concentrated thiosulphate solution (carrying out simultaneously a control experiment) a liberation of nearly 0·9 mol. of iodine per mol. of dibromide was registered in each case. The time taken was about 7 hours.

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