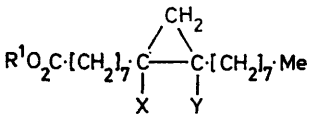
Reactions of Fatty Cyclopropenoids with Hydrogen Halides and Halogens

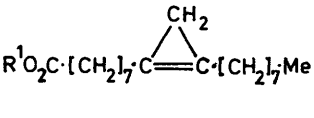
By D. A. Rosie and G. G. Shone,* School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames, Surrey

The additions of hydrogen halides and halogens to the cyclopropenoid ring of methyl sterculate have been shown to produce ring-opened and/or cyclopropanoid compounds. The composition of the products of these reactions has been determined quantitatively by n.m.r. and oxidative techniques. It is suggested that ring-opened compounds are formed by polar addition whereas halogenocyclopropanoids are produced by radical addition.

THE formation of the monobromo-compounds (I; $R^1 = X = H$, $Y = Br$ and $R^1 = Y = H$, $X = Br$) by the hydrohalogenation of sterculic acid (II; $R^1 = H$), has been reported by Fawcett and Smith.[1] From their results these authors concluded that it is surprising that the polymerisation of sterculic acid, involving attack of the cyclopropenoid ring of one molecule, by the acidic proton of a second molecule, results in the breaking of the cyclopropenoid ring.

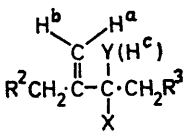


(I)

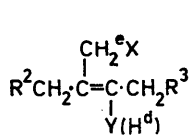


(II)

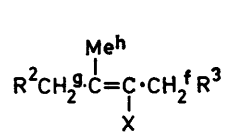
It has been known for some time that the hydrochlorination and hydrobromination of sterculic acid esters, during the determination of total cyclopropenoids [2] at temperatures up to 55°, give significant yields of ring-breakdown products of types (III) and (IV) (X = Br or Cl, Y = H) as determined by i.r. analysis,[3] and that treatment with acetic acid also yields ring-opened products.[4,5] We have now carried out a quantitative assessment of the products of reactions between the hydrogen halides and methyl sterculate (II; $R^1 = Me$), with particular reference to the possible formation of halogenocyclopropanoid material and of the third possible type of ring-breakdown product (V).



(III)



(IV)



(V)

R^2 = $MeO_2C\cdot[CH_2]_6$ or $Me\cdot[CH_2]_6$

R^3 = $[CH_2]_6\cdot Me$ or $[CH_2]_6\cdot CO_2Me$

Treatment of methyl sterculate with equimolar quantities of aqueous hydrogen chloride, hydrogen chloride in benzene, or hydrogen bromide in benzene, gave mixtures of products which proved impossible to separate by chromatographic means. I.r. studies on the total reaction products showed the presence of structures (III) and (IV) [X = Cl or Br, Y = H],[2,3] and new n.m.r signals were observed in the region τ 4·95 (s), 5·13 (s), and 5·62 (t), characteristic of H^a, H^b, and H^c of (III), and τ 4·48 (t) and 6·05 (s) due to H^d and H^e of (IV). Permanganate–periodate oxidation and determination of the formaldehyde produced, using chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid), confirmed the presence of (III).

Quantitative determination of compounds (III) and (IV) in the total reaction products was made by comparison of the areas of the resonances in the regions τ 4·95 and 5·13, and at τ 6·05, with the area of the ester methyl resonance at τ 6·35 (s). Table 1 shows that such

TABLE 1

Reaction between methyl sterculate and the hydrogen halides

	Products (%)		
Reagent solution	(III)	(IV)	(V)
(1) HCl–H_2O	61	25	14 * (9·8)
(2) HCl–C_6H_6 †	55 (51·0)	31	14 * (13·8)
(3) HBr–C_6H_6 †	69 (63·3)	21	10 * (11·0)
(4) HBr–C_6H_6 ‡	53	29	18 * (21·0)
(5) HBr–C_6H_6 §	39	47	14 *

* By difference: figures in brackets are oxidative data. † Extraction carried out < 20°. ‡ Evaporation carried out < 20°. § Evaporation carried out at 45°.

calculations accounted for all but 14% of the products in the case of hydrochlorination and 10—18% in the case of hydrobrominations. There was no indication of the presence of significant quantities of the halogenocyclopropanes (I; $R^1 = Me$, X/Y = H, Y/X = Cl or Br) in the i.r. spectra of the total products (absence of modification at $\nu_{max.}$ 1030 cm^{-1} to the skeletal vibration at 1020 cm^{-1} associated with the methyl ester group).

The third possible type of ring-opened structure (V; X = Cl or Br) would be expected to give n.m.r. signals in the regions τ 7·3—7·7 (H^f), 7·95 (H^g), and 8·5—8·7 (H^h). Modifications to the complex resonance at τ 7·7—7·9 ($CH_2\cdot C{=}C$ and $CH_2\cdot CO_2R$) were observed at τ 7·65 and to the chain methylene resonance (τ 8·70) in the regions τ 8·2—8·4. These minor complexities could be due to the presence of structure (V).

That structure (V) was the third and only remaining product of these reactions was confirmed by the per-

[1] R. F. Fawcett and J. C. Smith, *Chem. and Ind.*, 1960, 871.
[2] F. C. Magne, J. A. Harris, and E. L. Skau, *J. Amer. Oil Chemists' Soc.*, 1963, **40**, 716, 718.
[3] A. V. Bailey, F. C. Magne, G. J. Boudreaux, and E. L. Skau, *J. Amer. Oil Chemists' Soc.*, 1963, **40**, 69.
[4] K. L. Rinehart, jun., S. I. Goldberg, C. L. Tarimu, and T. P. Culbertson, *J. Amer. Chem. Soc.*, 1971, **83**, 225.
[5] H. W. Kircher, *J. Org. Chem.*, 1964, **29**, 1979.

manganate–periodate oxidation of the total reaction products and the detection and quantitative determination of the decan-2-one produced, by g.l.c. (Table 1).

No interconversion of the products of hydrochlorination [(III), (IV), and (V); X = Cl, Y = H] was observed at temperatures up to 55°, but the percentage composition of the hydrobromination products varied with the conditions, work-up procedure, and storage conditions (Tables 1 and 2), there being a tendency for larger quantities of the thermodynamically more stable isomer (IV; X = Br, Y = H) to be produced at higher temperatures at the expense principally of isomer (III).

The hydrochlorination and hydrobromination of methyl sterculate in benzene were complete after 25 min at 20 °C. The addition of hydrogen chloride or bromide

TABLE 2

Storage of methyl sterculate–hydrogen bromide products [a]

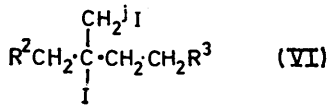
	Products (%)		
t/h	(III)	(IV)	(V)
0	39	47	14
168	26	58	16
288	23	61	16
13 months *	22	60	18

[a] Medium CCl_4; temperature 55°.

* Stored at 20° after initial 288 h at 55°.

to the initially formed halogenoalkenes, did not occur over prolonged periods at room temperature in the presence of excess of reagent. However, completely saturated products were formed on heating the bromoalkenes with hydrogen bromide–benzene at 55° in a sealed tube for 48 h.

Reaction between equimolar quantities of methyl sterculate and hydrogen iodide in benzene solution took place within 2 min at room temperature. The isolated mixture gave new i.r. absorption bands at $\nu_{max.}$ 880 [H_2C=C of (III; X = I, Y = H)], 1155 (skeletal), and 1640 (C=C stretch) cm^{-1}, and new n.m.r. signals at τ 4·66 (s), 4·79 (s), characteristic of H^a and H^b of (III; X = I, Y = H), and τ 4·34 (t) and 6·09 (s) due to H^d and H^e of (IV; X = I). In addition, small signals at τ 7·59 and 9·26 indicated that some cyclopropenoid structure remained, even though all the hydrogen iodide had been consumed. This could be explained by postulating the addition of hydrogen iodide to the initially formed halogenoalkenes, and it is possible that a major resonance which occurs at τ 6·14 is due to H^j of (VI).



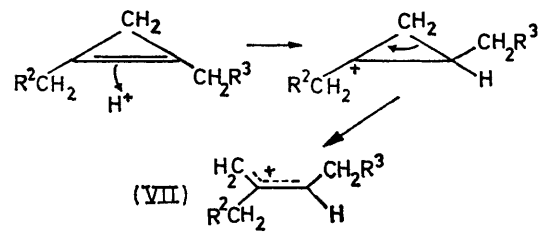
(VI)

That such a reaction occurs readily was demonstrated by adding hydrogen iodide–benzene to the original products of the methyl sterculate–hydrogen iodide reaction. Structure (III; X = I, Y = H), which was present to an extent of 23% of the initial products, represented only 6% of the total mixture 2 min after the addition of a second quantity of hydrogen iodide.

The presence of significant quantities of iodocyclopropanoids was not detected at any stage during these reactions (absence of modification at $\nu_{max.}$ 1030 cm^{-1} to the skeletal vibration at 1020 cm^{-1} associated with the methyl ester group).

Reactions between methyl sterculate and hydrogen chloride in aqueous medium, and methyl sterculate and hydrogen chloride, hydrogen bromide, and hydrogen iodide in benzene, gave the same types of ring-opened products. As reaction with hydrogen chloride in both water and benzene gave the same products in similar proportions, it seems reasonable to suppose that hydrohalogenation of methyl sterculate in benzene proceeds by a polar mechanism.

The products (III) and (IV) may be regarded as being formed by electrophilic addition to the double bond, resulting in ring breakdown and formation of an allyl cation (VII).



The formation of (V) may be formally explained by postulating proton addition to the σ bond of the cyclopropene ring (in the plane of the ring), but it is possible that addition takes place over the top of the ring by interaction with the overlapping sp–sp^2 orbitals of the Walsh model.[6]

The possibility of a radical mechanism occurring was investigated by carrying out the reaction between methyl sterculate and hydrogen bromide in benzene, in the presence of initiators and inhibitors. The addition of small quantities of dibenzoyl peroxide and dimethylaniline, and also di-isopropyl peroxydicarbonate did not increase the rate of hydrogen bromide uptake. No increase in rate was observed when the methyl sterculate–hydrogen bromide reaction was carried out under low intensity u.v. light. The addition of phenothiazine or galvinoxyl did not reduce the reaction rates, but hydrogen bromide was taken up by the galvinoxyl. These observations suggest that a radical reaction was not taking place.

The formation of only ring-opened products by electrophilic addition of the hydrogen halides to methyl sterculate is contrary to the observations reported by Fawcett and Smith,[1] but is supported by the production of alkenes of similar structural types by the polymerisation of sterculic acid,[4] and by treatment of sterculene with acetic acid.[5]

As only ring-opened products are formed when fatty cyclopropenoids undergo polar reactions, it is perhaps surprising that Fawcett and Smith [1] isolated dibromosterculic acid (I; R^1 = H, X = Y = Br) by treatment

[6] A. D. Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179.

of sterculic acid (II; R^1 = H) with bromine in chloroform at 0°.

We have now shown that ring-opened dihalogenoalkenes [(III) and (IV); X = Y = Br] are produced, in addition to the dihalogenocyclopropanoid structure (I; R^1 = Me, X = Y = Br), when methyl sterculate (II; R^1 = Me) is treated with bromine under these conditions.

The quantities of (III) (25%) and (IV) (45%) (X = Y = Br) produced when 1 mol. equiv. of bromine in chloroform was added slowly to methyl sterculate in the same solvent, were determined by comparing the n.m.r. signals at τ 4·56 (s), 5·07 (s), and 6·02 (s), characteristic of H^a, H^b (III), and H^e (IV) respectively, with the ester methyl resonance at τ 6·35 (s) [Table 3, (1)]. As all the cyclopropenoid reactant was destroyed (absence of n.m.r. signals at τ 7·59 and 9·26 and i.r. absorption at 1009 cm^{-1}) it would appear that the only other possible addition product, the dibromocyclopropanoid (I; X = Y = Br), accounted for the remaining 30% of the products. The occurrence of new n.m.r. signals at τ 8·35 and 8·65, which can be attributed to methylene protons α to the ring of (I), and a modification at 1040 cm^{-1} to the skeletal vibration at 1020 cm^{-1} (associated with the methyl ester group) in the i.r. spectrum, are indicative of a dihalogenocyclopropanoid structure. No dibromocyclopropanoid was produced when the bromine was added rapidly to the methyl sterculate solution [Table 3, (2)].

TABLE 3

Reaction between methyl sterculate and the halogens

	Halogen solution (1% w/v)	Reaction temperature (°)	t/min	Products (mol %) (I)	(III)	(IV)
(1)	Br_2–$CHCl_3$ *	1	5	30	25	45
(2)	Br_2–$CHCl_3$ *	1	<5	0	21	79
(3)	I_2–CCl_4 *	50	30	100	0	0
(4)	IBr–CCl_4 *	0	~50	55	14	31
(5)	ICl–CCl_4 *	40	~30	54	23	23
(6)	Cl_2–CCl_4 *	1	2	20	46	17
(7)	IBr–CCl_4 †	20	~30	70	5	25
(8)	IBr—CCl_4 ‡	20	>1020	30	7	56

* Carried out in diffuse daylight. † Carried out in sunlight. ‡ Carried out in darkness in the presence of phenothiazine (0·4%).

The iodination of methyl sterculate in carbon tetrachloride, benzene, toluene, and dioxan gave only the diiodocyclopropanoid structure (I; R^1 = Me, X = Y = I), no alkenyl material being observed in the n.m.r. or i.r. spectra of the products. The n.m.r. spectrum showed a new triplet at τ 8·31 (J 7 Hz) due to methylene protons α to the cyclopropanoid ring, a resonance in the region τ 8·60 (on the side of the aliphatic chain methylene proton resonance) characteristic of a *trans*-di-iodocyclopropanoid,[7] and a small resonance at τ 9·05 attributable to the presence of a small quantity of *cis*-isomer.[7] An absorption at 1040 cm^{-1} in the i.r. spectrum confirms the presence of a dihalogenocyclopropanoid structure.

The composition of the total products obtained by the halogenation of methyl sterculate, in diffuse daylight, using iodine monobromide or iodine monochloride, is given in Table 3 [(4) and (5)]. In each case *ca.* 55% of the corresponding dihalogenocyclopropanoids were formed.

When chlorine was slowly added to a solution of methyl sterculate in carbon tetrachloride at 1°, until all the cyclopropenoid ring was destroyed (as determined by the disappearance of the n.m.r. signal at τ 9·26), slightly more than 1 mol. equiv. of reagent was consumed. Quantitative analysis by n.m.r. spectroscopy showed that the products of this reaction contained 46% of the terminal alkene (III; X = Y = Cl) and 17% of the tetra-substituted alkene (IV; X = Y = Cl). The addition of the excess of reagent to the initially-formed halogenoalkenes gave 17% of polychlorinated compounds, indicating the production of 20% of dichlorocyclopropanoids. The presence of approximately this level of dihalogenocyclopropanoids in the total products, was confirmed by i.r. spectroscopy (modification at $\nu_{max.}$ 1040 cm^{-1} to the skeletal vibration at 1020 cm^{-1}). The n.m.r. spectrum contained a shoulder at τ 8·38, which could be attributable to the methylene protons α to the ring in (I; R^1 = Me, X = Y = Cl) or to the presence of polychlorinated material.

Visible light was necessary for the reaction between methyl sterculate and iodine to proceed, and removal of the source of irradiation resulted in the cessation of the reaction. The addition of 0·4% of the radical reaction inhibitor phenothiazine resulted in a 50-fold decrease in reaction rate (determined spectrophotometrically). E.s.r. studies confirmed the presence of radicals during reaction with iodine in solution. As only one type of product was formed by reaction between methyl sterculate and iodine it would appear that radical addition to the cyclopropenoid ring results in cyclopropanoid formation.

In contrast, the reaction between methyl sterculate and bromine proceeded rapidly in the absence of light but was partially inhibited by the presence of phenothiazine (determined spectrophotometrically). It would appear that the reaction is mainly polar in character, leading to the production of dibromoalkenes, with a competing radical reaction also taking place which results in dibromocyclopropanoid material being formed [Table 3, (1)]. This is supported by the lack of formation of dibromocyclopropanoids when the bromine reagent was added rapidly[8] [Table 3, (2)], and that cyclopropyl radicals are more stable and have less tendency to ring-open than cyclopropyl cations.

That a polar mechanism leads to ring-opened products, and a radical pathway to dihalogenocyclopropanoids, was supported by examination of the reaction between methyl sterculate and iodine monobromide. When 1 mol. equiv. of iodine monobromide was added to methyl sterculate in the presence of sunlight, reaction was complete in 30 min and 30% of dihalogenoalkenes and 70% of dihalogenocyclopropanoid isomers were pro-

[7] K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, 1960, **82**, 6375.

[8] B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 1961, 80.

duced [Table 3, (7)]. The formation of large amounts of the dihalogenocyclopropanoids was confirmed by a strong characteristic absorption in the i.r. spectrum at $\nu_{max.}$ 1040 cm^{-1}. E.s.r. studies confirmed that a radical reaction was taking place, the signals being weaker than those obtained in the case of the iodination.

However, when the reaction was carried out in darkness in the presence of phenothiazine a small quantity of methyl sterculate remained after 17 h. The dihalogenoalkenes now comprised 63% and the dihalogenocyclopropanoids 30% of the products [Table 3, (8)], a complete reversal of the quantities previously obtained. The small amount of dihalogenocyclopropanoids was confirmed by i.r. studies.

Thus it would appear that radical addition of the halogens to methyl sterculate leads to dihalogenocyclopropanoids whereas polar addition results in ring breakdown. Reaction between methanethiol and methyl sterculate in benzene has been reported to give only cyclopropanoid material and it has been suggested that this reaction proceeds by a radical pathway.[9]

EXPERIMENTAL

Benzene and toluene were dried over sodium wire. Carbon tetrachloride was distilled twice from phosphorus pentoxide. Chloroform was freed from ethanol by shaking three times with water and was dried over molecular sieve. Dioxan was passed down a silicic acid column before use. Light petroleum had b.p. 40—60°. ^1H N.m.r. spectra were obtained using a Perkin-Elmer R10 60 MHz instrument, with tetramethylsilane as internal or external standard. I.r. spectra were obtained on liquid films between rock salt plates, using a Unicam SP 200 or a Perkin-Elmer 457 spectrophotometer. Visible absorption measurements were obtained using a Unicam SP 600 spectrophotometer. Mass spectra were obtained on A.E.I. MS2 and MS9 instruments (electron beam energies 30—70 eV) using a direct insertion probe at 200°. E.s.r. spectra were obtained at room temperature, on a Varian E3 spectrometer, for benzene or carbon tetrachloride solutions. Vapour pressure osmometry was carried out on a Hewlett–Packard F2M series 301A instrument using toluene as solvent and a probe temperature of 65°. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-1B instrument with a rate of temperature increase of 4° min^{-1}. G.l.c. was carried out on a Philips PV4000 instrument fitted with flame ionisation detectors and 2 m × 2 mm stainless steel columns. Nitrogen was used as carrier gas. Solutions of hydrogen halides were prepared by passing the appropriate purified reagent into dry, nitrogen-purged organic solvents. Methyl sterculate was isolated by urea clathration of the mixed methyl esters of *Sterculia foetida* seed fat. Removed means removed under reduced pressure at temperatures < 20°. ' Dried ' means dried with magnesium sulphate.

Methyl Sterculate with Aqueous Hydrogen Chloride.—Methyl sterculate (120 mg) was shaken with concentrated hydrochloric acid (*d* 1·18) (40 ml) for 1 h, under a nitrogen atmosphere at 20°. Water was added and the products were extracted twice with light petroleum. The combined extracts were washed with water until free from acid, dried, and the solvent was removed to yield 130 mg of mixed products (III), (IV), and (V) (X = Cl, Y = H), $\nu_{max.}$ 720 (–$[CH_2]_n$–), 820 and 880 (–C–C–O–), 905 (=CH_2), 1020 (C–CO–OMe), 1100, 1170, 1200, and 1245 (C–O), 1360 and 1435 (–Me), 1460 (–CH_2–), 1637 (C=C), 1740 (C=O), and 2851 and 2920 (C–H) cm^{-1}, τ 4·48 [t, =CH of (IV)], 4·95 and 5·13 [2 × s, =CH_2 of (III)], 5·62 [t, =C·CHCl of (III)], 6·05 [s, CH_2Cl of (IV)], 6·40 (s, CO_2Me), 7·70—7·90 (m, CH_2·C=C and CH_2·CO_2R), 8·30—8·50 [m, CH_2·CCl of (III) and ClC=C·Me of (V)], 8·70 (CH_2), and 9·10 (t, CMe).

Methyl Sterculate with Hydrogen Chloride or Hydrogen Bromide in Benzene (Typical Procedure).—Methyl sterculate (106 mg) in benzene (5 ml) was treated with a 0·1M solution of hydrogen halide in benzene (20 ml) at 20° for 20 min. The products were isolated either by the addition of aqueous sodium hydroxide and extraction with light petroleum [Table 1, (2) and (3)] or by removal of the solvent and excess of reagent [Table 1, (4) and (5)]. Products showed similar i.r. and n.m.r. spectra to the methyl sterculate–aqueous hydrogen chloride products.

Oxidations.—Oxidations were carried out using a modified Lemieux–von Rudloff method,[10] with sodium metaperiodate (20·86 g) and 0·01M-aqueous potassium permanganate (250 ml) made up to 1 l with water.

(i) *Determination of* (V). A 0·25% aqueous solution of potassium carbonate (10 ml) was mixed with the periodate–permanganate reagent (20 ml) and water (30 ml), t-butyl alcohol (30 ml), heptyl methyl ketone (10 mg), methyl nonyl ketone (10 mg) and the sample to be oxidised (125 mg) [dissolved in t-butyl alcohol (10 ml)]. After shaking for 90 min, enough solid sodium metabisulphite was added to discharge the colour of the initially formed iodine. The mixture was extracted with diethyl ether (3 × 40 ml). The ether extracts were combined, washed with water (2 × 10 ml), dried, and filtered. The ether solution was concentrated by blowing dry nitrogen over the surface at room temperature, and was examined by g.l.c. (10% Carbowax MW1000 on 80—100 mesh Chromosorb W at 125°, and 3% SE-30 on 80—100 Chromosorb W at 120°). The areas of the ketone peaks were determined using a planimeter, and the percentage of (V) found. The response factor of each individual ketone was found to be unity.

(ii) *Determination of* (III). Hydrochlorinated and hydrobrominated products (130 mg) were oxidised for 18 h as in (i), the t-butyl alcohol being replaced by water (30 ml). Portions of the products (5 ml) were mixed with 1M-solutions of sodium arsenite (2 ml), and sulphuric acid (2 ml), and with water (1 ml). The presence of formaldehyde was shown by the production of a violet colouration when an aliquot portion (0·2 ml), diluted with water (0·8 ml), was treated with chromotropic acid (10 ml).[10] Quantitative determination of (III) was made by measuring the absorbance of the formaldehyde–chromotropic acid colouration at 570 nm and comparing this with a calibration curve (prepared by treating known amounts of formaldehyde with the chromotropic acid).

Addition of Hydrogen Bromide to the Methyl Sterculate–Hydrogen Bromide Products.—Products isolated from the methyl sterculate–hydrogen bromide reaction [Table 1, (4)] (98 mg) were mixed with a 0·4M solution of hydrogen bromide in benzene (20 ml) and the solution was sealed in a Pyrex tube. The solution was heated at 55° for 48 h and the solvent and excess of reagent were removed, the yield of products being 116 mg. No olefinic protons could be

[9] H. W. Kircher, *J. Amer. Oil Chemists' Soc.*, 1964, **41**, 4.
[10] R. U. Lemieux and E. von Rudloff, *Canad. J. Chem.*, 1955, **33**, 1701.

observed in the n.m.r. spectrum of the products, and the i.r. absorption bands at $\nu_{max.}$ 905 (=CH_2) and 1637 (C=C) cm^{-1} in the starting material had disappeared.

Isomerisation of (III; X = Br, Y = H) *to* (IV; X = Br, Y = H).—Monohydrobrominated products of methyl sterculate (125 mg), dissolved in carbon tetrachloride (0·3 ml) were sealed in an n.m.r. sample tube and maintained at 55°. The solution was examined by n.m.r. spectroscopy at various times (Table 2).

Methyl Sterculate with Hydrogen Iodide in Benzene.—A 0·07M solution of hydrogen iodide in benzene (2·6 ml) was added to a nitrogen-purged solution of methyl sterculate (56 mg) in benzene (3 ml) at 20°. After two minutes the solvent was removed, the yield of mixed products (II), (III), (IV), (VI), and probably (V) (X = I, Y = H) being 81 mg. The i.r. spectrum above 700 cm^{-1} was similar to that obtained for the hydrochlorinated products except that an additional absorption band occurred at 1155 cm^{-1} (C=C·CH_2I). N.m.r. signals occurred at τ 4·35 [t, =CH of (IV)], 4·66 and 4·79 [2 × s, =CH_2 of (III)], 5·16 [t, =C·CHI of (III)], 6·09 [s, CH_2I of (IV)], 6·14 [s, CH_2I of (VI)], 6·40 (s, CO_2Me), 7·59 (m, cyclopropene-CH_2), 7·70—7·90 (m, CH_2·C=C and CH_2CO_2R), 8·30—8·50 [m, CH_2·CI of (III) and IC=CMe], 8·70 (CH_2), 9·10 (t, CMe), and 9·26 (cyclopropene CH_2).

A portion of the products (70 mg) was dissolved in benzene (5 ml) and 0·07M-hydrogen iodide in benzene (0·4 ml) added, at 20°. After two min, the products were isolated as before, the yield being 72 mg. The n.m.r. spectrum was identical to that recorded previously except for the disappearance of the τ 7·59 and 9·26 resonances and the appearance of a signal at τ 8·30.

Methyl Sterculate with Bromine in Chloroform [*Table* 3, (1)].—Methyl sterculate (236 mg) was dissolved in chloroform (22 ml) and the solution cooled to 1°. A 1% solution (w/v) of bromine in chloroform (16·8 ml), at 1°, was added to the methyl sterculate solution over a period of 5 min with stirring. The solvent was removed, the yield of [(I), (III), and (IV) (X = Y = Br)] as a yellowish oil being 347 mg, $\nu_{max.}$ 575 and 670 (C–Br), 720 ([CH_2]$_n$), 820 and 880 (C–C–O–), 905 (=CH_2), 1020 (C–CO–O–Me), 1040 (cyclopropyl), 1100, 1170, 1200 and 1245 (C–O), 1360 and 1435 (–Me), 1460 (–CH_2–), 1631 (C=C), 1740 (C=O), and 2851 and 2920 (C–H), τ 4·56 and 5·07 [2 × s, =CH_2 of (III)], 6·02 [s, CH_2Br of (IV)], 6·35 (s, CO_2Me), 7·70—7·90 (m, CH_2·C=C and CH_2·CO_2R), 8·30—8·60 [m, CH_2·CBr of (III) and CH_2–cyclopropyl–CH_2 and *trans*-cyclopropyl CH_2 of (I)], 8·70 (CH_2), 9·05 [*cis*-cyclopropyl CH_2 of (I)], and 9·10 (t, CMe).

Methyl Sterculate with Bromine in Chloroform [*Table* 3 (2)].—A 1% solution of bromine in chloroform (6·5 ml) at 1° was added to a stirred solution of methyl sterculate (119 mg) in chloroform (12 ml) at 1°, over a period of 20 s. The mixture was left for 5 min. The solvent was removed, the yield of (III) and (IV) (X = Y = Br) as a yellowish oil being 176 mg. The absence of i.r. absorption bands at $\nu_{max.}$ 670 and 1040 cm^{-1} and n.m.r. signals at τ 8·30—8·60 and 9·05 compared with the previous bromination suggests that no dibromocyclopropanoid compound (I; X = Y = Br) had been formed.

Methyl Sterculate with Iodine [*Table* 3, (3)].—A 1% solution of iodine in carbon tetrachloride (25 ml) at 50° was added over 30 min to a solution of methyl sterculate (282 mg) in carbon tetrachloride (26 ml) at 50°. The solution was cooled and the solvent removed, the yield of *methyl di-iodosterculate* being 502 mg. Identical material was obtained using a reaction time of *ca.* 150 min in benzene, toluene, or dioxan at 20°. The i.r. spectrum was similar to that obtained for the products of the reaction between methyl sterculate and bromine in chloroform [Table 3, (1)] except that the absorption band at 670 cm^{-1} was replaced by a band at 535 cm^{-1}, and the bands at 575 and 1631 cm^{-1} were absent. N.m.r. signals occurred at τ 6·35 (s, CO_2Me), 7·80 (t, CH_2·CO_2R), 8·31 (t, CH_2–cyclopropyl–CH_2), 8·65 (*trans*-cyclopropyl CH_2), 8·70 (CH_2), 9·05 (*cis*-cyclopropyl CH), and 9·10 (t, CMe) [Found: *M* (vapour pressure osmometry), 571. $C_{20}H_{36}I_2O_2$ requires *M*, 562], *m/e* 308 (*M* – I_2), 254 (I_2^+), 128 (HI^+), and 127 (I^+) (in other respects identical to methyl sterculate), decomposition point (differential scanning calorimetry), 190°.

Methyl Sterculate with Iodine Monobromide in Carbon Tetrachloride [*Table* 3, (4)].—A 1% solution of iodine monobromide in carbon tetrachloride (12 ml), at 0°, was added to a solution of methyl sterculate (177 mg) in carbon tetrachloride (5 ml) at 0°, over 30 min. The solution was shaken with 0·1N-sodium thiosulphate (10 ml) and water (3 × 10 ml), dried, and filtered. The solvent was removed to yield [(I), (III), and (IV) (X/Y = I, Y/X = Br)] (285 mg). The i.r. spectrum above 720 cm^{-1} was similar to that obtained for the products of the reaction between methyl sterculate and bromine in chloroform [Table 3, (1)] except that the absorption band at 905 cm^{-1} was replaced by a band at 913 cm^{-1}. N.m.r. signals were obtained at τ 4·56, 5·05, 6·02, 6·35, 7·70—7·90, 8·31, 8·65, 8·70, 9·05, and 9·10 (assignments as above). A similar addition of iodine monobromide was carried out in the dark in the presence of phenothiazine.

Methyl Sterculate with Iodine Monochloride in Carbon Tetrachloride [*Table* 3, (5)].—A 1% solution of iodine monochloride in carbon tetrachloride (9 ml) at 40°, was added to a solution of methyl sterculate (169 mg) in carbon tetrachloride (17 ml) at 40°, over 25 min.

The solvent and excess of reagent were removed, the products [(I), (III), and (IV) (X/Y = I, Y/X = Cl)] (245 mg) showing $\nu_{max.}$ 720, 760, 820, 880, 913, 1020, 1040, 1100, 1170, 1200, 1245, 1360, 1435, 1460, 1620, 1740, 2851, and 2920 cm^{-1}, τ 4·55, 5·02, 5·98, 6·35, 7·60—7·90, 8·35, 8·65, 8·70, 9·00, and 9·10 (assignments as before).

Methyl Sterculate with Chlorine in Carbon Tetrachloride (*Table* 3, (6)].—Methyl sterculate (100 mg) dissolved in carbon tetrachloride (10 ml) was cooled to 1°. A 0·5% solution of chlorine in carbon tetrachloride (1·5 ml) at 1° was added and the solution stirred for 2 min and monitored by n.m.r. spectroscopy. Further quantities of the chlorine solution were added (2 × 1·5 ml and 2 × 0·5 ml) until the resonance at τ 9·26 (due to cyclopropene CH_2) had disappeared. The products showed $\nu_{max.}$ 720, 800, 820, 880, 908, 1020, 1040, 1100, 1170, 1200, 1245, 1360, 1435, 1460, 1631, 1740, 2851, and 2920 cm^{-1} and τ 4·52, 4·98, 5·95, 6·35, 7·60—7·90 (m), 8·38, 8·60, 8·70, and 9·10 (t) (assignments as before).

We thank the Tropical Products Institute for a studentship (to D. A. R.), Varian Associates Limited for e.s.r. facilities, and the S.R.C. for financial assistance.

[1/932 *Received*, 8*th June*, 1971]