bronze, Russian workers[7] have noted the formation of ferrocene in this modified Ullmann process. The reaction been repeated several times in this laboratory—each run giving rise to a significant amount of ferrocene in addition to biferrocenyl (Table II), even under conditions slightly milder than those previously reported.[7,9]

TABLE II

PRODUCTS FROM TREATMENTS OF IODOFERROCENE (20 G., 0.064 MOLE) WITH ACTIVATED COPPER BRONZE AT 90° DURING 24 HR. UNDER NITROGEN

	Biferrocenyl[a]		Ferrocene[a]	
Run	Grams	% Yield[b]	Grams	% Yield[b]
1	7.50	63.4	2.80	23.7
2	7.50	63.4	2.90	24.3
3	8.20	69.4	2.50	20.9

[a] Data obtained from purified products. [b] Calculations based on complete conversion of iodoferrocene.

Experimental[25]

Biferrocenyl from Silylferrocenes.—Isolation of biferrocenyl from the complex reaction mixtures obtained from treatment of lithioferrocenes with trialkylbromosilanes may be illustrated by one such procedure in which tri-*n*-hexylbromosilane was used. After preparation of a mixture of lithio- and dilithioferrocene by reaction of ferrocene (18.0 g., 0.097 mole) with *n*-butyllithium (0.71 mole), and then treatment with tri-*n*-hexylbromosilane (35.0 g., 0.096 mole), the reaction mixture was prepared for distillation as previously described.[2] Distillation was carried through collection of a forerun [150–165° (0.2 mm.)] and then collection of tri-*n*-hexylsilylferrocene [184–187° (0.05 mm.)]. At pot temperature of 200–220° (0.05 mm.) biferrocenyl appeared as an orange colored, crystalline sublimate in the column. After all of the material had sublimed and the apparatus was allowed to cool to room temperature, the sublimate was washed out in chloroform solution. Evaporation of the chloroform yielded 170 mg. of crude biferrocenyl (0.11% yield based on 0.097 mole of ferrocene). Initial purification, accomplished by chromatography on alumina and evaporation of the elution solvent, benzene, afforded reasonably pure biferrocenyl. Constant melting material (227.5–229.0°) was obtained, however, only after repeated recrystallizations from benzene–petroleum ether (b.p. 40–50°). Melting range determinations of biferrocenyl were carried out in carefully evacuated capillary tubes since decomposition of the compound (pure or slightly impure) usually started near 200° in the presence of air.

Anal. Calcd. for $(C_{10}H_9Fe)_2$: C, 64.91; H, 4.90; Fe, 30.19; mol. wt., 372. Found: C, 65.03; H, 5.08; Fe, 30.39; mol. wt. (cryoscopic), 385, 389 (camphor), and 397, 361 (naphthalene).

Ferrocene *via* Thermal Decomposition of Tri-n-hexylsilylferrocene.—Tri-*n*-hexylsilylferrocene[2] (5.00 g., 10.7 moles) was slowly heated in a 100-ml. flask fitted with an air condenser. The amber-colored fluid started to darken at about 220°, and decomposition proceeded rapidly near 250°. During the rapid period of the decomposition a mass of orange colored, crystalline material sublimed into the air condenser. The sublimate was collected and shown to be ferrocene (16% yield) by means of comparison of infrared spectra and by admixture melting with authentic material. An ultraviolet spectrum of the sublimate also was found to be identical with that of ferrocene. It did not exhibit any of the intense absorption characteristic of the presence of biferrocenyl.[4]

Similar treatment of another sample of tri-*n*-hexylsilylferrocene except that heating was carried out in an atmosphere of purified nitrogen, merely caused the material to reflux gently with no sign of decomposition.

Biferrocenyl and Ferrocene from Iodoferrocene.[26]—Iodoferrocene (20 g., 0.064 mole), prepared by means of treatment of chloromercuriferrocene[27] with iodine in methylene dichloride solution according to the procedure reported by Shechter and Helling,[8] and activated copper bronze[28] (40 g.) were intimately mixed and placed into a 100-ml. Kjeldahl flask. The flask and contents were flushed with purified nitrogen during 30 min. at room temperature, and then maintained under a slight head of nitrogen during 20 hr. while the system was heated at 90°. Some of the ferrocene formed during the reaction could be seen sublimed on the neck of the flask after several hours. When the reaction mixture had been allowed to cool to room temperature it was extracted with 15-ml. portions of warm benzene until the extracts appeared colorless. Evaporation of the combined extracts *in vacuo* yielded a mass of crystalline material which was dissolved in hot hexane and the resulting solution allowed to cool to room temperature. The initial crop of crystalline material was collected, and the supernatent reduced slightly in volume. This caused a second crop of crystalline material to be deposited which was collected, and again the volume of the supernatent reduced. By repeating this procedure many times it was possible to effect a clean separation between biferrocenyl and ferrocene, the former being less soluble in hexane. Individual crops were each recrystallized from hexane giving, in this representative run, purified biferrocenyl (7.5 g., 63.4%) and purified ferrocene (2.9 g., 24.3%) which each gave rise to infrared and ultraviolet spectra identical to those obtained from respective authentic samples.

TABLE III

COMPOUNDS USED

Compound	9-Band	10-Band
Ferrocene	9.012	9.942
Biferrocenyl	8.986	9.985
m-Tolylferrocene	9.029	9.978
Diferrocenylketone	9.025	9.971
2-Biphenylylferrocene	9.034	9.942
α-Hydroxyethylferrocene	9.036	9.977
Diferrocenylmercury	9.029	9.979
Palmitoylferrocene	9.027	9.976
Hexadecylferrocene	9.036	9.983
Chloromercuriferrocene	9.037	9.990
Trimethylsilylferrocene	9.025	9.975
Benzoylferrocene	9.019	9.963
Benzylferrocene	9.035	9.979
p-Phenoxyphenylferrocene	9.031	9.978
Acetylferrocene	8.996	9.968

Infrared Measurements.—All of the compounds examined (Table III) were samples of analytical purity. Measurements were carried out with a Perkin-Elmer Model 21 double beam recording spectrophotometer, equipped with a sodium chloride prism interchange unit. Absorption intensity data were recorded at the wave lengths given in Table III, with slit settings of 0.0212 and 0.0282 μ at 9 and 10 μ, respectively. Measurements were made from several concentrations (usually four) of each ferrocene derivative in solutions of purified carbon disulfide. The same liquid absorption cell of 1-mm. thickness was used throughout the study. Absorbences were calculated with the use of base lines[15] drawn in each case as nearly parallel as possible to the background radiation of the solvent. Background radiation was checked before and after a series of runs.

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[25] All temperature readings are uncorrected. Analysis by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weight determinations by the Huffman Microanalytical Laboratories, Wheatridge, Colo.

[26] Procedure based upon those previously reported.[7,9]

[27] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk, SSSR*, **97**, 459 (1954).

[28] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 188.

Preparation of Bicyclo[4.3.1]dec-7-en-10-one

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Although bicyclo[4.3.1]dec-7-en-10-one has not been reported, the preparation of a few derivatives has been accomplished by alkylation of carbethoxycycloheptanone with either 1,3-dichloro-2-butene or 1-chloro-3-butanone followed by ring closure at the other α-carbon to give 1-carbethoxy-7-methylbicyclo[4.3.1]dec-7-en-10-one and the corresponding acid.[1]

Similarly, 1-carbethoxy-4-methylbicyclo[3.3.1]non-3-en-9-one and its acid, as well as the derivatives of larger carbethoxycycloalkanones, have been prepared.[1] Other bicyclo[3.3.1]nonane derivatives have become available through alkylation of carbethoxycyclohexanone with β-chloropropionaldehyde or β-chloropropionaldehyde diethyl acetal.[2,3]

Substitution of a methyl group for the carbethoxy group has also been shown to permit formation of a substituted bicyclo[3.3.1]nonane system.[4] When, however, the carbethoxy group or the methyl group is not present, cyclization preferentially is accomplished by reaction with the carbonyl group of the cyclic ketone rather than by reaction with the α-hydrogen. 2-(3-Chlorocrotyl)cycloheptanone, for example, gave bicyclo-[5.4.0]undec-7-en-9-one,[1] and 2-(3-chlorocrotyl)cyclohexanone gave 45% of $\Delta^{1(9)}$-2-octalone and a trace of 4-methylbicyclo[3.3.1]non-3-en-9-one.[4] Examination of models indicates that the tendency to react with the α-hydrogen on the opposite side of the carbonyl carbon would be enhanced greatly if the 3-chlorocrotyl group is maintained in an axial position. Since, when there is neither a methyl nor a carbethoxy group present on the same α-carbon, the 3-chlorocrotyl group most likely would assume an equatorial position, it is reasonable that cyclization then would take place by reaction with the more accessible carbonyl group if a reaction path is available.

The use of 1,3-dichloropropene instead of 1,3-dichloro-2-butene for the preparation of bicyclic compounds offers the same advantages of an allyl halogen for the alkylation of the carbethoxycyclohexanone together with a vinyl halogen, inert in the initial alkylation but available for the later sulfuric acid-induced cyclization. Furthermore, 2-(3-chloroallyl)cycloheptanone does not have a methyl group available for reaction with the carbonyl group when the carbethoxygroup is absent, and the alternate mechanism of ring closure, therefore, is not available.

That the use of 1,3-dichloropropene is indeed a satisfactory method of preparing bicyclic compounds was established by preparation of the known 1-carbethoxybicyclo[3.3.1]non-3-en-9-one.[2] Once it was demonstrated that the method would work, 2-carbethoxy-2-(3-chloroallyl)cycloheptanone was prepared and stirred with sulfuric acid. Chromatographic analysis of the product mixture before distillation established the presence of a little 2-(3-chloroallyl)-cycloheptanone in addition to higher boiling materials. The heat of the fractional distillation, however, resulted in the formation of a compound not present before distillation. The new compound was identified as bicyclo[4.3.1]dec-7-en-10-one, derived from the loss of the carbethoxy group of the 1-carbethoxybicyclo-[4.3.1]dec-7-en-10-one formed in the cyclization.[5]

The preparation of bicyclo[4.3.1]dec-7-en-10-one from 2-(3-chloroallyl)cycloheptanone, however, proved to be a more economical method.[6] This preparation served both as a proof of structure of the product and as a means of establishing that the product resulted from the decarbethoxylation of 1-carbethoxybicyclo[4.3.1]-dec-7-en-10-one during fractionation, rather than from the cyclization of 2-(3-chloroallyl)cycloheptanone present before, or formed during distillation. The 2-(3-chloroallyl)cycloheptanone was fractionated through the same stainless steel sponge-packed column as the product mixture from the reaction of 2-carbethoxy-2-(3-chloroallyl)cycloheptanone without formation of any bicyclo[4.3.1]dec-7-en-10-one.

The identity of the products of the two methods was established by boiling points, refractive indices, identical gas chromatographic traces individually or mixed, and finally by mixture melting points and infrared spectra of their 2,4-dinitrophenylhydrazones.

Experimental[7]

Starting Materials.—1,3-Dichloropropene was obtained by the method of Hill and Fischer,[8] starting with epichlorohydrin (Eastman White Label) and by careful fractionation of "Flashed D-D" (Shell Chemical Co.). Both sources gave a chromatographically pure material that contained approximately equal quantities of the *cis* and *trans* isomers. Carbethoxycyclohexanone (Arapahoe Chemicals, Inc.) and cycloheptanone (Aldrich Chemical Co.) are available commercially. Carbethoxycycloheptanone was prepared from cycloheptanone and diethyl oxalate[9] (Eastman White Label) and carefully fractionated through a 23 × 1.5-cm. stainless steel sponge packed column to give a chromatographically pure liquid boiling at 105° (3 mm.), $n^{26}\text{D}$ 1.4685.

2-Carbethoxy-2-(3-chloroallyl)cyclohexanone.—Carbethoxycyclohexanone (170 g., 1 mole) was added to a hot solution of sodium (23 g., 1 g.-atom) in 700 ml. of absolute alcohol. When the initially formed solid went into solution, 1,3-dichloropropene (111 g., 1 mole) was added to the hot solution, and the mixture was left to reflux overnight. The mixture then was filtered and the alcohol removed by distillation. The residue was taken up in ether, washed with water, and left to dry over magnesium sulfate. Distillation[10] gave 127.9 g. (52.4%) of liquid boiling 146–164° (5 mm). Careful fractionation through the stainless steel sponge-packed column gave a chromatographically pure liquid boiling 148–154° (5 mm.), $n^{25}\text{D}$ 1.4471.

Anal. Calcd. for $C_{12}H_{17}ClO_3$; C, 58.90; H, 6.94. Found: C 58.91; H, 6.98.

Bicyclo[3.3.1]non-3-en-9-one-1-carboxylic Acid 2,4-Dinitrophenylhydrazone.—2-Carbethoxy-2-(3-chloroallyl)cyclohexanone (2.4 g.) was carefully laid on the surface of 10 ml. of concentrated sulfuric acid and left to stand at room temperature for 5 days. The mixture then was poured into ice–water and extracted with ether. The ether solution was washed with sodium bicarbonate solution and water and dried over magnesium sulfate. The residue[11] remaining after removal of ether was refluxed overnight with 10% hydrochloric acid. The mixture was then cooled, taken up in ether, and washed with sodium bicarbonate solution.

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(1) V. Prelog, P. Barman, and M. Zimmerman, *Helv. Chim. Acta*, **32**, 1284 (1949).

(2) A. C. Cope and M. E. Synerholm, *J. Am. Chem. Soc.*, **72**, 5228 (1950).

(3) A. C. Cope and E. S. Graham, *ibid.*, **73**, 4702 (1951).

(4) S. A. Julia, *Bull. soc. chim. France*, 780 (1954).

(5) This decarbethoxylation was not altogether unexpected in view of similar experiences in the distillation of carbethoxycyclohexanone and carbethoxycycloheptanone in this laboratory and the not unrelated reversal of the condensation of nitromethane with cyclohexanone on distillation, T. F. Wood and R. J. Cadorin, *J. Am. Chem. Soc.*, **73**, 5504 (1951).

(6) Preliminary work with 2-(3-chloroallyl)cyclohexanone indicates a similar course of reaction with the formation of bicyclo[3.3.1]non-3-en-9-one.

(7) Melting and boiling points are not corrected. Microanalyses by Wieler and Strauss, Oxford.

(8) A. J. Hill and E. J. Fischer, *J. Am. Chem. Soc.*, **44**, 2582 (1922).

(9) H. R. Snyder, L. A. Brooks, and S. H. Shapiro, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.

(10) The crude material contains 2-(3-chloroallyl)cyclohexanone.

(11) Chromatographic analysis showed the reaction to be only about half complete. Most chromatographic analyses were done with a homemade unit with a 6-ft. column of Dow-Corning silicone stopcock grease on Johns-Manville Chromosorb at 200° with helium as the carrier gas. Several of the analyses were checked with a Perkin-Elmer vapor fractometer Model 154, using column R, polypropylene glycol.

Evaporation of the ether extract of the acidified sodium bicarbonate solution left a small (about 0.5 g.) residue which was taken up in alcohol and treated with the 2,4-dinitrophenylhydrazine reagent.[12] The resulting 2,4-dinitrophenylhydrazone, recrystallized from alcohol, m.p. 257–259 dec., gave no depression of melting point when mixed with an authentic sample.[13]

2-Carbethoxy-2-(3-chloroallyl)cycloheptanone.—Carbethoxycycloheptanone (31.3 g., 0.17 mole) was added to a hot solution of sodium (3.19 g., 0.17 g.-atom) in 100 ml. of absolute alcohol. After half an hour of heating, 1,3-dichloropropene (18.9 g., 0.17 mole) was added, and the mixture was left to reflux overnight. The usual work up followed by distillation gave 21 g. (47.7%) of colorless liquid boiling at 135–150° (4 mm.). Careful fractionation through the stainless steel sponge-packed column gave a chromatographically pure liquid boiling at 129° (1 mm.), $n^{23}\text{D}$ 1.4858.

Anal. Calcd. for $C_{13}H_{19}ClO_3$: C, 60.36; H, 7.34. Found: C, 60.42; H, 7.65.

2-(3-Chloroallyl)cycloheptanone.—Cycloheptanone (112 g., 118 ml., 1 mole) was added to a well stirred mixture of sodium amide (40 g., 1.02 moles) in 500 ml. of anhydrous ether. The mixture was refluxed for 4 hr. and then cooled in ice–water, with nitrogen flowing through the system, and treated with a solution of 1,3-dichloropropene (111 g., 1 mole) in 100 ml. of anhydrous ether. When the initial exothermic reaction had subsided, the mixture was left to reflux overnight. The mixture was then cooled and 500 ml. of water was added. The ether solution was washed with water and dried over magnesium sulfate. Distillation gave 25 g. of unchanged cycloheptanone and 86.8 g. (59.2%) of liquid boiling at 125–130° (10 mm.). Careful fractionation gave a chromatographically pure analytical sample boiling at 96° (2 mm.), $n^{22}\text{D}$ 1.4978.

Anal. Calcd. for $C_{10}H_{15}OCl$: C, 64.36; H, 8.04. Found: C, 64.46; H, 8.09.

Bicyclo[4.3.1]dec-7-en-10-one.—(a) 2-Carbethoxy-2-(3-chloroallyl)cycloheptanone (41.6 g., 0.16 mole) was added dropwise with stirring to 50 ml. of concentrated sulfuric acid. After the mixture had been stirred for 1 week at room temperature, the reaction was stopped by the addition of 500 ml. of cold water and the product was taken up in ether. The ether was washed with sodium bicarbonate solution[14] and water and dried over magnesium sulfate. Chromatographic analysis after removal of the ether revealed the presence of a little 2-(3-chloroallyl)cycloheptanone but no bicyclo[4.3.1]dec-7-en-10-one. Fractionation yielded 5.25 g. (21.7%) of bicyclo[4.3.1]dec-7-en-10-one,[15] boiling 100–105° at (4 mm.), $n^{24}\text{D}$ 1.5020, 2,4-dinitrophenylhydrazone m.p. 136–138, containing only a trace of 2-(3-chloroallyl) cycloheptanone and 10.9 g. of an inseparable[16] mixture[17] of starting material and 1-carbethoxybicyclo[4.3.1]dec-7-en-10-one boiling at 145–150° (4 mm.), $n^{24}\text{D}$ 1.4896.

(b) 2-(3-Chloroallyl)cycloheptanone (49 g., 0.263 mole) was added to 50 ml. of concentrated sulfuric acid and worked up as before. Chromatographic analysis of the product before distillation indicated approximately an equal mixture of unchanged starting material and product. Distillation gave 5.5 g. (14%) of good quality bicyclo[4.3.1]dec-7-en-10-one[18] boiling at 85–91° (2 mm.), $n^{23}\text{D}$ 1.5050, 2,4-dinitrophenylhydrazone, m.p. 136–138°. There was no depression of melting point on mixture with the 2,4-dinitrophenylhydrazone obtained from method a.

Acknowledgment.—This research was supported by a grant from The Alfred University Research Foundation.

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(12) Shriner and Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948, p. 171.

(13) Reported (ref. 2) 259–261°, dec.

(14) Only a trace of gummy material was obtained by acidifying the sodium bicarbonate solution.

(15) Bicyclo[4.3.1]dec-7-en-10-one begins to polymerize after only a few days at room temperature.

(16) With the available fractionating equipment.

(17) No trace of either 2-(3-chloroallyl)cycloheptanone or bicyclo[4.3.1]-dec-7-en-10-one was present in this fraction. A second distillation, with a purposely prolonged total reflux, however, resulted in contamination from both these materials.

(18) An 18.3-g. sample (46.4%) of liquid (of which the 5.5 g. was the best), slightly contaminated with 2-(3-chloroallyl)cycloheptanone, was actually isolated. Greater yields of highly pure product would be possible with better fractionating equipment.

Cyanoethylation of Butadiene Sulfone

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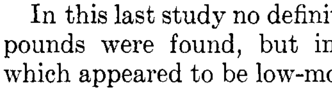
Although cyanoethylation of aryl sulfones[1] and 1,3,5-trimethylene trisulfones[2] has been described, the reaction of butadiene sulfone with acrylonitrile was reported to take another course.[3]

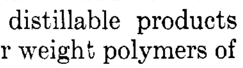
In this last study no definite crystalline addition compounds were found, but instead distillable products which appeared to be low-molecular weight polymers of acrylonitrile and butadiene sulfone. Copolymers of acrylonitrile and cyclic sulfones, containing at least 85% acrylonitrile, also have been claimed.[4]

This paper reports the preparation of a crystalline adduct by the base-catalyzed reaction of butadiene sulfone and four moles of acrylonitrile. It was postulated to be 2,2,5,5-thiophenetetrapropionitrile 1-dioxide (I) on the basis of analysis, infrared spectrum, and chemical behavior. Unlike previous products,[3] our product decomposed at the melting point, with evolution of gas, to form a new crystalline solid. Analysis, infrared and ultraviolet spectra, showed the new compound to be 1,4-tetrakis(2′-cyanoethyl)-1,3-butadiene [better name: 4,7-bis(2′-cyanoethyl)-4,6-decadienedinitrile] (II). The thermal decomposition of I into II constitutes strong evidence of the postulated structures, in view of the known[5] breakdown of simple diene sulfones into 1,3-dienes upon heating.

This two-step procedure provides a new method of preparing 1,4-substituted 1,3-dienes.



I



$$\begin{array}{l} HC{=}C(CH_2CH_2CN)_2 \\ | \\ HC{=}C(CH_2CH_2CN)_2 \end{array}$$

II

Experimental[6]

2,2,5,5-Thiophenetetrapropionitrile-1,1-dioxide (I).—To a solution of 11.8 g. (0.10 mole) of butadiene sulfone (from the Phillips Petroleum Co.), 23.3 g. (0.44 mole) of acrylonitrile, and 50 ml. of acetonitrile was added a mixture of 1 g. of acetonitrile and 2 g. of a 40% solution of benzyltrimethylammonium hydroxide in methanol over a period of 3.5 hr. at 0–10°. The mixture was neutralized with acetic acid and filtered. The product (20% yield) was recrystallized from acetonitrile to give white crystals melting at 209.5–210°, decomposing with the evolution of gas.

Anal. Calcd. for $C_{16}H_{18}N_4O_2S$: C, 58.16; H, 5.49; N, 16.96; S, 9.70. Found: C, 58.40; H, 5.72; N, 17.53; S, 9.57.

Its infrared spectrum showed bands at 2255 cm.$^{-1}$ (nitrile), 1425 cm.$^{-1}$ ($-CH_2CN$), 1295 and 1130 cm.$^{-1}$ (sulfone), 958 and

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(1) H. A. Bruson (to the Resinous Products and Chemical Co.), U. S. Patent 2,435,552 (February 3, 1948).

(2) H. T. Hookway and E. M. Evans (to British Resins Products Ltd.), U. S. Patent 2,468,015 (April 19, 1949).

(3) R. Wegler and H. Lafos (I. G. Leverkusen), 1944; referred to by O. Bayer, *Angew. Chem.*, **61**, 229 (1949).

(4)(a) A. Fournet and H. Lemoine (to Societe des Usines Chimiques Rhone-Poulenc) U. S. Patent 3,017,397 (January 16, 1962); (b) NOTE ADDED IN PROOF.—After this manuscript had been accepted, news of the preparation of compound I was received [Derwent, British Patent, Abstract 3, no. 5, Gp. 1, 2 (February 1, 1963)].

(5)(a) Badische Anilin- and Soda-Fabrik, German Patent 236,386; *Chem. Zentr.*, **II**, 316 (1911); (b) O. Grummitt, A. E. Ardis, and J. Fick, *J. Am. Chem. Soc.*, **72**, 5167 (1950).

(6) Melting points are corrected.