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Structure and Properties of 2,2-Dibromovinyl Trifluoromethyl Ketone

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Abstract—It was established by IR spectroscopy and quantum-chemical calculations along nonempirical DFT method in B3LYP version with the basis set 6-311 G(d,p) that 2,2-dibromovinyl trifluoromethyl ketone consisted of a mixture of *s-cis* planar conformer and *s-trans*-form deviating from a plane by 13°, whereas the *s-cis*-form is more energetically stable than the *s-trans* one (ΔE –5.07 kcal mol^{-1}). Also in 2,2-dibromovinyl methyl ketone the planar *s-cis* conformer is more stable. Chlorine-containing analogs, 2,2-dichlorovinyl trifluoromethyl ketone and 2,2-dichlorovinyl methyl ketone, are more stable in the planar *s-trans*-conformation. Charge distribution and polarization in the dibromovinyl ketones are analogous to those in dichlorovinyl ketones in agreement with the established reactivity of dibromovinyl trifluoromethyl ketone. By reaction of 2,2-dibromovinyl trifluoromethyl ketone with 2,4-dinitrophenyl-, alkylhydrazines, *N,N*-dimethylhydrazine, N,N-, N,O-, N,S-binucleophiles were respectively obtained hydrazone, derivatives of pyrazole, imidazole, oxazole, and 1,3-thiazine containing a trifluoromethyl group.

We have reported [1] on the synthesis of 2,2-dibromovinyl trifluoromethyl ketone (**I**) by trifluoroacetylation of 1,1-dichloroethene in the presence of aluminum bromide. Prior to our investigations ketones with a dibromovinyl group were not known, and their structure and characteristics were not studied.

In the present work were investigated the chemical properties and structure of 2,2-dibromovinyl trifluoromethyl ketone and a comparative analysis was made of structural parameters and reactivity of this compound and alkyl, aryl, and trifluoromethyl 2,2-dichlorovinyl ketones [2].

We formerly investigated the conformational structure of important organic synthons, alkyl(aryl) 2,2-dichlorovinyl ketones by using quantum-chemical calculations SCF MO LCAO by semiempirical method CNDO/2, calculating atomic vibrations by measuring permettivity, IR, UV, ^{1}H NMR, ^{35}Cl NQR spectra [2–5]. It was established that aliphatic derivatives existed as mixtures of two planar *s-cis*, *s-trans* conformers, and aromatic 2,2-dichlorovinyl ketones were present as planar *s-cis* forms. It was also demonstrated that the structures of ketones and their 2,4-dinitrophenylhydrazones govern the cyclization process of the latter into pyrazoles and also the biological activity thereof [6–8].

In this study the structure of 2,2-dibromovinyl trifluoromethyl ketone (**I**), trifluoromethyl 2,2-dichlorovinyl ketone (**II**), and conformational equilibrium in these molecules were investigarted by means of ^{1}H NMR and IR spectroscopy and by quantum-chemical calculations by method DFT in a version B3LYP/6-311 G (d,p) (Tables 1, 2). For the sake of comparison analogous nonempirical quantum-chemical calculations were also performed (Table 2) for methyl 2,2-dichloro(dibromo)vinyl ketones (**III, IV**). The results obtained were compared with previous calculations for methyl 2,2-dichlorovinyl ketone (**III**) carried out by CNDO/2 procedure [5].

In the ^{1}H NMR spectrum of 2,2-dibromovinyl ketone (**I**) a singlet is observed from the α-proton shifted downfield by 0.6 ppm as compared with a singlet from the vinyl proton in the ^{1}H NMR spectrum of its 2,2-dichlorovinyl analog (**II**) and by 1.2–0.6 ppm relative to the position of the olefin proton signal for alkyl, aryl 2,2-dichlorovinyl ketones [2]. The larger value of the chemical shift from the signal of olefin proton in the ^{1}H NMR spectrum of ketone **I** (Table 1) is in agreement with the known increase in the chemical shift value for the proton in position *2* at introduction of a bromine in position *1* of ethane as compared with 1-chloroethenes [9]. The presence in vibrational spectra of trifluoromethyl 2,2-dibromo-

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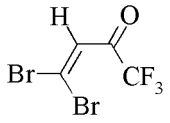
Table 1. IR and ^{1}H NMR spectral data for groups C=C, C=O, and =CH of dibromo(dichloro)vinyl ketones

Compd.	ν, cm^{-1} (CCl_4)		ν, cm^{-1} (microfilm)			δ, ppm ($CDCl_3$)
	C=C	C=O	=C–H	C=C	C=O	=CH
$CF_3C(O)CH=CBr_2$ (**I**)	1528	1677, 1780	3055	1563	1731, 1743 shoulder	7.63
$CF_3C(O)CH=CCl_2$ (**II**)	1572.9	1734, 1782	3065	1574	1733, 1781	7.00
$CH_3C(O)CH=CCl_2$ (**III**)	1574	1676, 1705	3050	1576	1674, 1704	6.45
$C_6H_5C(O)CH=CCl_2$	1557	1657	3060	1570	1670	7.17

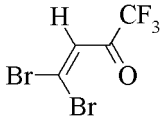
Table 2. Total charges, bond lengths, dipole moments, and bond energy in *s-cis*- and *s-trans*-conformations of dihalovinyl ketones

Compd. no.	Rotamer	μ, D	$-E_{total}$, ppm	*E*, kcal mol^{-1}	Charges				Bond length, nm			
					C	C	C_{carb}	O	C=O	C–C	C=C	C–CX_3
I	B 0°	2.4	5676.1756742	–5.07	–0.25	–0.07	0.11	–0.25	120.5	147.4	134.2	155.6
	A 166.7°	2.4	5676.1675874	0	–0.26	–0.05	0.08	–0.25	120.8	148.1	134.2	155.5
II	B 0o	2.3	1448.3339650	–4.36	–0.19	–0.04	0.11	–0.25	120.5	147.2	134.1	155.6
	A 180°	2.2	1448.3270224	0	–0.23	–0.01	0.08	–0.25	120.8	147.7	134.2	155.4
III	B 0°	2.7	1150.5343024	0.32	–0.18	–0.07	0.19	–0.29	121.2	149.0	133.9	152.2
	A 180°	1.9	1150.5348083	0	–0.24	–0.01	0.20	–0.29	121.5	149.3	133.6	151.2
IV	B 0o	2.6	5378.3771545	–0.96	–0.23	–0.09	0.20	–0.29	121.1	149.5	133.8	151.8
	A 180°	2.1	5378.3756207	0	–0.27	–0.06	0.20	–0.29	121.6	149.7	133.7	151.1

(dichloro)vinyl ketones (**I, II**) of a doublet in the absorption region of C=O group (Table 1) similarly to the spectra of alkyl dichlorovinyl ketones is likely to originate from existence thereof as two rotary *s-cis*-, *s-trans*-conformers [4, 5].



A *s-trans*



B *s-cis*

In the IR spectrum of ketone **I** a shift is observed of the stretching bands of the carbonyl group and the double bond to the region of higher frequencies, and therewith a reverse of their intensity occurs compared with the corresponding bands and intensities for alkyl, aryl, and trifluoromethyl 2,2-dichlorovinyl ketones [1, 2, 4, 5]. Therewith in the IR spectra of ketones **I** and **II** the frequencies of bands corresponding to groups C=O and C=C differ little likely because of dominating inductive effect of the trifluoromethyl group.

According to performed calculations 2,2-dibromovinyl trifluoromethyl ketone (**I**) and its dichlorovinyl analog **II** consist of a mixture of conformers: ketone **II** of planar *s-cis*- and *s-trans*-forms, ketone **I** of planar *s-cis*- and deviating from a plane by 13° *s-trans*-form (Table 2). Thus the observed significant increase in the chemical shift of the olefin proton signal in the spectrum of ketone **I** (Table 1) compared to that in ketone **II** also may be caused by the existence of dibromoketone **I** molecule in the nonplanar *s-trans*-conformation hampering the conjugation between the double C=O and C=C bonds.

The most energetically feasible form for dibromovinyl ketone **I** and 2,2-dibromovinyl methyl ketone (**IV**) is the *s-cis*-conformer whereas for their chloro-substituted analogs **II, III** these are *s-trans*-conformers (Table 2). Energy parameters of ketones **I, II, IV** conformers differ considerably.

At the same time the difference in the total energy of conformers of methyl dichlorovinyl ketone **III** ($\Delta E = E_{s\text{-}trans} - E_{s\text{-}cis} = 0.32$ kcal mol^{-1}) indicates comparable stability of *s-cis*- and *s-trans*-conformers of this compound in contrast to the previously obtained [5] by CNDO/2 values that have suggested the higher energetical stability of the *s-trans*-conformer ($\Delta E = 5.27$ kcal mol^{-1}).

It was demonstrated that the lengths of C=C, C_∞–C_{carb}, C=O, C–CF_3 (CH_3) bonds were almost independent of the conformational structure of ketones **II–IV**, only a small elongation of the C_{carb}–C_{methyl} bond is observed in the *s-cis*-isomer of methyl dichlorovinyl ketone (**III**). In the *s-cis*-, *s-trans*-conformers of ketone **I** the difference in the length of C=C, C=O, C–CF_3 (CH_3) bonds is also insignificant, but in its nonplanar *s-trans*-conformer a considerable elongation of C–C_{carb} bond is observed evidencing increased conjugation between the double bond and the carbonyl group in this conformation of ketone **I**.

The charges on the atoms calculated for various conformations of dichlorovinyl ketone **II** and ketones **III, IV** are considerably different unlike almost equal bond lengths.

The replacement of a methyl group by a trifluoromethyl one results in decrease in ketones **I, II** of the negative charge on the oxygen of the carbonyl group compared to that in the nonfluorinated analogs **III, IV** in keeping with the large electronegative effect of the trifluoromethyl group. However it also leads to reduction in the positive charge on the carbon atom of the carbonyl group.

Atoms C_β in compounds **I–IV** of both conformations are negatively charged, and the absolute charge value is greater in the dibromovinyl derivatives.

In both conformers of trifluoromethyl ketone **I** the charges on atoms C_β and O are almost equal (Table 2). At the same time in methyl 2,2-dichlorovinyl and 2,2-dibromovinyl ketones **III, IV**, and in ketone **II** the highest electron density is located on the oxygen of the carbonyl group (Table 2). The charges on carbon atoms of the double bond C_α and C_β in two conformers of nonfluorinated methyl 2,2-dibromovinyl ketone **IV** and methyl 2,2-dichlorovinyl ketone **III** are notably different, and only the oxygens of the carbonyl groups have the same negative charge.

The comparison of calculation results for methyl 2,2-dichlorovinyl ketone obtained by CNDO/2 [5] and by nonempirical method used in this study show considerable difference in the values of bond lengths and in their polarization depending on the calculation procedure used. For instance, it was shown before [5] that C_β atom is less positively charged than the carbon of the carbonyl group. In this study calculations evidence that the double bond in β,β-dihalovinyl ketones is polarized in direction of the C_β carbon.

The dipole moments calculated *ab initio* also are in better agreement with the experimental data for methyl 2,2-dichlorovinyl ketone [5].

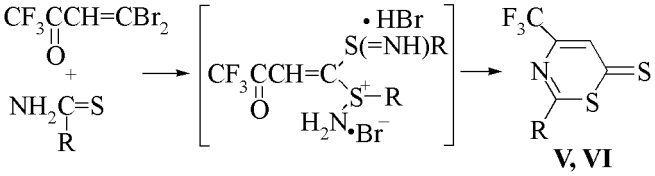
All the above stated testifies to the similar charge distribution and polarization of C=C and C=O bonds in compounds **I–IV**, and consequently dibromovinyl ketones **I, IV** should behave in reactions with nucleophiles analogously to ketones **II, III**.

The reactivity of dibromovinyl trifluoromethyl ketone found in this study supports the above conclusion.

2,2-Dibromovinyl trifluoromethyl ketone as trifluoromethyl 2,2-dichlorovinyl ketone [2] is extremely promising for preparation of polyfunctional heteroatomic and heterocyclic compounds containing a trifluoromethyl group. Compounds with a perfluoromethyl group, especially those belonging to heterocyclic series, exhibit high biological activity, and some among them are applied as pharmaceuticals, herbicides etc. [10, 11].

Reactivity of ketone **I** was investigated by examples of reactions with acetylthioamide, thiourea, *o*-phenylenediamine, *o*-aminophenol, 2,4-dinitrophenylhydrazine, and alkylhydrazines.

Reactions of ketone **I** with thiourea and thioacetamide in alcoholic media at the reagents ratio 1 : 2 gave rise to 1-amino- and 1-methyl-1,3-thiazine-6-thiones (**V, VI**) respectively in up to 70% yield.



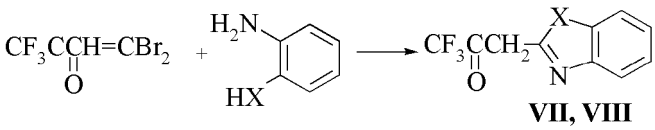
V, VI

R = NH_2 (**V**), CH_3 (**VI**).

The arising compounds **V, VI** are similar to thiazines obtained by reaction of 2,2-tricloromethyl ketone **II** with thiourea and thioacetamide [2].

Reaction of ketone **I** with *o*-phenylenediamine is similar to that of compound **II** and occurs with simultaneous substitution of geminal bromine atoms and heterocyclization into 2-(trifluoroacetonyl)benzimidazole (**VII**), whose properties and structure has been described in detail before [2].

Analogously the exothermic reaction of ketone **I** with *o*-aminophenol proceeded with replacement of



VII, VIII

X = NH (**VII**), O (**VIII**).

Table 3. Yields, melting points, IR and NMR spectral data for compounds **I, V**–**XI**

Compd. no.	Yield, %	mp, °C (bp, °C)	IR spectra (in pellets with KBr and microfilm), ν, cm^{-1}	^1H, ^{19}F, ^{13}C NMR spectra, solvent, δ, ppm, J, Hz
I	74	(146)	1047–1333 (CF_3) [15], 1563 (C=C), 1729 (C=O), 3055 (=C-H)[a]	$CDCl_3$: 1H: 7.63 (=CH); ^{19}F: –79.80 (CF_3)$_b$; ^{13}C: 116.48 (=CBr_2), 115.22 q (CF_3, J_{C-F} 291.3), 125.59 (=CH), 175.97 q (C=O, J_{C-CF} 36.9)
V	68	177–179	1290 (C=S), 1490, 1560, (C=C), 1635 (C=N), 3100 (=C–H), 3285 (NH_2)	CD_3OD: 6.85s (=CH), ^{19}F –70.15 s (CF_3)[b]
VI	78	53–55	1300 (C=S), 1510, 1590 (C=C, C=N), 2930, 2970 (CH3), 3045 (=C–H), 2925, 2970 (CH_3)	CD_3OD: 7.23 s (1H, =CH), 2.61 s (3H, CH_3); ^{19}F –69.93 s (CF_3)[b]
VII	71	289–290	1480(C=C), 1600 (C=N), 1635 (C=O), 3040, 3080 (=C-H), 2650–2930 (NH-, C_{alk}–H), 3250 (N–H)	DMSO-d_6: 7.50 m, 7.20 m (5H, C^7H_5), 5.40 (1H, =CH), 12.0 (NH)
VIII	98	186	1320, 1340, 1510, (NO_2), 1620 (C=N), 3060, 3100 (=C-H), 3270 (NH) 8.34 d, 9.34 d (C_6H_3, J 10)	DMSO-*d*6: 6.39 s (=CH), 9.46 (NH), 7.52 d, 8.34 d, 9.34 d (C6H3, J 10)
IX	61	(145)	1060–1230 (CF_2–F) [15], 1470 (C=C), 2960 (CH_3), 3150 (=C–H)[b]	CD_3Cl: 3.91 s (3H, NCH_3), 6.47 s (1H, =CH); ^{19}F –63.40 s (CF_3)[b]
Xc	56	([c])	1465, 1570 (C=C, C=N), 3145 (=C–H) 6.52 (1H, =C^4–H)	1.44 t (3H, CH_3), 4.24 q (2H, NCH_2) (J 11.64),
XI	85	158[d]	1090–1230 (CF_3) [15], 1470, 1530, 1580, 1620 (C=C, C–N, C=N), 1640 (C=O), 3160 (N–H)	6.06 s (1H, =C-H), 7.34 m, 7.49 d, 7.58 d (J 7.0) (2H, 1H, 1H, C^7H_4), 10.05 br (1H, OH), ^{19}F –75.26 (CF_3)[b]

[a] IR spectra recorded from microfilm of substance.

[b] Chemical shift in the spectrum determined relative to CCl_3F.

[c] The product purified by column chromatography.

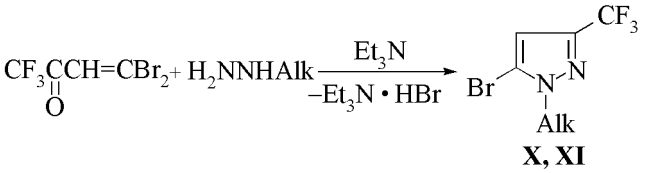
[d] Publ. [13]: mp 202–205°C (Table), 165–166°C (EXPERIMENTAL).

halogen atoms and formation of 2-(trifluoroacetonyl)-benzoxazole (**VIII**) in 85% yield. The reaction was carried out at equimolar reagents ratio in alcohol in the presence of 2 equiv of alkali.

Benzoxazole **VIII** was obtained formerly [12] in 80% yield at heating *o*-aminophenol with fluoroacetyldiethoxyketene for 3 h at 90–95°C. Taking into account the accessibility of ketone **I**, milder conditions of the process, and higher yield of the target product the developed procedure for preparation of benzoxazole **VIII** has significant advantages before the known method [12].

In the IR, ^1H and ^{13}C NMR spectra were observed signals indicating that compound **VIII** exists in solid state as ketone and in solution as enol (Table 3). Thus in the ^1H NMR spectrum appeared a singlet from the olefin proton, signals from the four protons of the benzoxazole ring, and a signal from a proton of OH group. The observed long-wave shift of the stretching vibrations band of the carbonyl group in the IR spectrum of 2-trifluoroacetonylbenzoxazole (**VIII**) reveals the presence of the hydrogen bonds.

In reaction with 2,4-dinitrophenylhydrazine ketone **I** affords the corresponding hydrazone **IX**. In contrast in the reaction of ketone **I** with alkylhydrazones we failed to isolate the corresponding hydrazones, and as reaction products formed 5-bromo-1-alkylpyrazoles **X, XI**. The reactions were carried out as well as at equivalent amounts of reagents and at the double excess of alkylhydrazine.

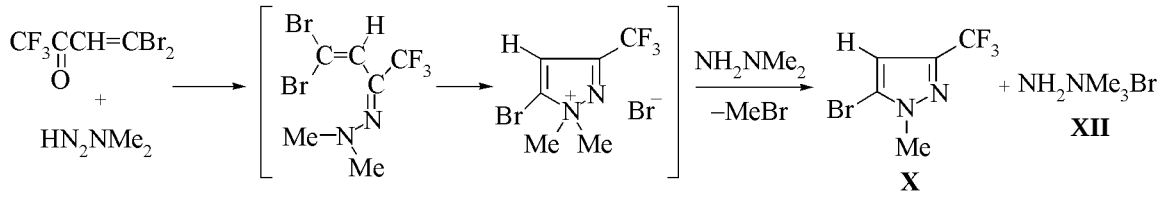


X, XI

Alk = CH_3 (**X**), C_2H_5 (**XI**).

The reaction between 2,2-dibromovinyl trifluoromethyl ketone (**I**) with 1,1-dimethylhydrazine resulted in formation of 5-bromo-1-methyl-3-trifluoromethylpyrazole (**X**) in 70% yield. The reaction was carried out in organic solvents at the reagents ratio 1 : 2 with

heat evolution. As the second reaction product was isolated 1,1,1-trimethylhydrazinium bromide (**XII**) in up to 90% yield. At equimolar ratio of reagents also was obtained pyrazole **X**, trimethylhydrazinium bromide, and unreacted 2,2-dibromovinyl ketone **I** was recovered. The likely reaction path consists first in formation of 2,2-dibromovinyl ketone di methylhydrazone followed by an intramolecular attack of the nucleophilic dimethylamine fragment on the β-carbon of the vinyl group. The arising *N*,*N*-dimethylpyrazolinium bromide under the action of 1,1-dimethylhydrazine suffers dequaternization into the target product with elimination of salt **XII**.



An alternative mechanism including the primary formation of a quaternary salt 1-[1-bromo-2-trifluoroacetylvinyl]-1,1-dimethylhydrazinium bromide followed by heterocyclization is hardly probable. This assumption is supported by formation of quaternary salts of dimethylhydrazine having similar structure: 1-[1-bromo-2-benzoyl(2-thenoyl)vinyl]-1,1,-dimethylhydrazinium bromides from the corresponding bromoacetylene ketones and 1,1-dimethylhydrazine whose structure has been determined by X-ray diffraction analysis [13]; these salts do not undergo cyclization into pyrazoles.

Thus the reaction of 2,2-dibromovinyl trifluoromethyl ketone with 1,1-dimethylhydrazine may be suggested as an efficient procedure for preparation of 5-bromo-1-methyl-3-trifluoromethylpyrazole, a very promising semiproduct for building up heterocyclic compounds possessing practically useful properties: pharmaceuticals, dyes, insectoacaricides etc. [10, 11]. The second product of this reaction, trimethylhydrazinium bromide, is of interest as a biologically active substance and an aminating reagent [14].

The structure of products prepared from 2,2-dibromovinyl trifluoromethyl ketone was proved by physicochemical methods, by elemental analysis, and also for compounds **V**–**VIII** by comparison of their physicochemical parameters (Table 3) with the data of these compounds obtained before [2, 12].

Thiazinethiones **V, VI** are yellow or orange powders with a characteristic odor. Their IR and ^{1}H NMR spectra (Table 3) are similar to the spectra of thiazinethiones prepared previously from ketone **II** [2]. All characteristics of benzimidazole **VIII** are consistent with the published data [2].

In the IR spectrum of hydrazone **IX** appear the characteristic absorption bands of C=N, NO_2, and NH groups (Table 3). In the IR spectra of pyrazoles **X, XI** should be first of all mentioned an absorption band characteristic of 5-bromopyrazoles in the region 3140–3150 cm^{-1} (=CH). In the ^{1}H NMR spectra alongside the signals of alkyl groups appears also a singlet from the pyrazole ring proton H^4 at 6.52–6.54 ppm. In the spectrum of 5-choro analog of pyrazole **X** the signal of H^4 is observed at 6.47 ppm.

Thus we have demonstrated that 2,2-dibromovinyl trifluoromethyl ketone is a highly reactive polyfunctional reagent, and it can find wide application in the organic synthesis. Its chemical properties originate from the presence of highly reactive bromine and highly electrophilic carbonyl group. In reactions with ambidentate S,N-, N,N-binucleophiles and hydrazines both bromine atoms and the oxygen of carbonyl group can simultaneously undergo substitution generating respectively derivatives of 1,3-thiazine and pyrazole; in reaction with *o*-phenylenediamine and *o*-aminophenol only halogen atoms are replaced, and arise derivatives of benzimidazole and benzoxazole.

EXPERIMENTAL

^{1}H, ^{13}C, ^{15}N, ^{19}F NMR spectra were registered on spectrometers Bruker DPX-400 (at 400.6, 100.61, 376 MHz for 1H, ^{13}C, ^{19}F respectively) and Jeol FX-90 Q (at 90 and 84 MHz for ^{1}H and ^{19}F respectively), internal reference HMDS.

IR spectra were recorded on spectrophotometers Bruker IFS 25 and Specord 75IR from KBr pellets, microfilms, and from solutions in CCl_4.

In experiments was used molten aluminum bromide of "pure for analysis" grade.

2,2-Dibromovinyl trifluoromethyl ketone (I). To a dispersion of 40 g (0.15 mol) of $AlBr_3$ and 0.35 g of

anhydrous $FeCl_3$ in 150 ml of anhydrous ethyl bromide or dibromomethane at –50…–60°C was added through a bubbler 0.1 mol of trifluoroacetyl chloride or bromide, and to the mixture was added dropwise 12.6 g (0.12 mol) of vinylidene chloride. The reaction mixture was stirred for 3 h at –50… –60°C, then it was warmed to room temperature, and for 15 min it was maintained at 25–30°C. The reaction mixture was treated with ice, the water layer was extracted with chloroform, the organic solution was dried with $CaCl_2$ and distilled. Yield of ketone 21.1 g (75%) [1].

2-Amino-4-trifluoromethyl-1,3-thiazine-6-thione (V). To a solution of 1.52 g (0.02 mol) of thiourea in 50 ml of ethanol was added dropwise at stirring 2.81 g (0.01 mol) of 2,2-dibromovinyl trifluoromethyl ketone. On completion of heat evolution the stirring continued for 4 h at heating to 40°C. Then the reaction mixture was poured into cold water, the separated yellow flakes were filtered off and dried in a vacuum-desiccator. Yield of reaction product is 1.7 g. Found, %: C 27.79; H 1.72; N 13.25; S 29.60. $C_5H_3F_3N_2S_2$. Calculated, %: C 28.29; H 1.41; N 13.20; S 30.17.

2-Methyl-4-trifluoromethyl-1,3-thiazine-6-thione (VI). In 32 ml of methanol was dissolved at stirring 1.5 g (0.02 mol) of thioacetamide. To the solution was added dropwise 2.81 g (0.01 mol) of 2,2-dibromovinyl trifluoromethyl ketone. On completion of heat evolution the stirring continued for 3 h at heating to 50°C. Then the reaction mixture was poured into water, the separated precipitate was filtered off and dried in a vacuum-desiccator. Yield 1.05 g. Found, %: C 34.24; H 1.82; N 5.80; S 29.50. $C_6H_4F_3NS_2$. Calculated, %: C 34.12; H 1.91; N 6.63; S 30.36.

Trifluoroacetonylbenzimidazole (VII). To a solution of 1.12 g (0.01 mol) of *o*-phenylenediamine in 60 ml of anhydrous ethyl ether was added dropwise 2.81 g (0.01 mol) of 2,2-dibromovinyl trifluoromethyl ketone. On completion of heat evolution the stirring continued for 3 h. The separated precipitate of trifluoroacetonylbenzimidazolinium hydrobromide was treated with sodium carbonate solution, the obtained precipitate of compound **VII** was filtered off and dried. Yield 1.65 g. Found, %: C 52.37; H 3.42; N 12.14. $C_{10}H_7F_3N_2O$. Calculated, %: C 52.46; H 3.09; N 12.28.

Trifluoroacetonylbenzoxazole (VIII). To a solution of 1.1 g (0.01 mol) of *o*-aminophenol and 0.8 g (0.02 mol) of NaOH in 20 ml of methanol or ethanol was added dropwise 2.81 g (0.01 mol) of 2,2-dibromovinyl trifluoromethyl ketone in 5 ml of alcohol. On completion of heat evolution the stirring continued for 3 h. Then the reaction mixture was poured into water, the separated precipitate of benzoxazole was filtered off and dried in air. Yield 1.95 g. Found, %: C 52.64; H 2.29; F 24.68; N 6.58. $C_{10}H_6F_3NO_2$. Calculated, %: C 52.64; H 2.64; F 4.87; N 6.11.

2,4-Dinitrophenylhydrazone of 2,2-dibromovinyl trifluoromethyl ketone (IX). To a solution of 1.76 g (0.01 mol) of 2,4-dinitrophenylhydrazine in 15 ml of anhydrous methanol and 0.5 ml of concn. H_2SO_4 was added at stirring 2.81 g (0.01 mol) of ketone **I**. On completion of heat evolution the stirring continued for 15 min at heating to 60°C. The separated precipitate was filtered off and dried in a vacuum-desiccator. Yield 2.30 g Found, %: C 25.89; H 1.21; Br 34.39; N 12.05. $C_{10}H_5Br_2F_3N_4O_4$. Calculated, %: C 26.00; H 1.09; Br 34.59; N 12.13.

5-Bromo-1-methyl-3-trifluoromethylpyrazole (X). (a) To a solution of (0.02 mol) of methylhydrazine in 40–50 ml of anhydrous ether was added dropwise 5.62 g (0.02 mol) of dibromovinyl ketone **I**. The mixture self-heated, and a precipitate of methylhydrazinium bromide separated. On completion of heat evolution the stirring continued for 1–2 h, the methylhydrazinium bromide was filtered off, and from the filtrate on removing the solvents was isolated pyrazole **X** in 2.96 g (61%) yield. Found, %: C 26.18; H 1.64; N 12.09. $C_5H_4BrF_3N_2$. Calculated, %: C 26.22; H 1.76; N 12.23.

(b) To a solution of 1.20 g (0.02 mol) of *N*,*N*-dimethylhydrazine in 50–100 ml of anhydrous hexane or ether was slowly added dropwise 2.81 g (0.01 mol) of 1,1,1-trifluoro-4,4-dibromo-3-buten-2-one. On completion of heat evolution the stirring continued for 1–2 h. The separated precipitate of trimethylhydrazinium bromide **XII** was filtered off and dried in a vacuum over P_2O_5. Yield of the salt 1.35 g (87.5%), mp 238–242°C (decomp.). (Publ. [16]: mp 242°C with decomp, from MeOH–Me_2C=O). Found, %: C 32.58; H 10.24; Br 31.97; N 25.37. $C_3H_{11}BrN_2$. Calculated, %: C 32.58; H 10.03; Br 32.06; N 25.33. IR spectrum (in ¤Br), cm^{-1}: 3200, 3100, 3005, 2700 (NH), 2950 (CH_3), 1480, 1630 (C–N).

5-Bromo-1-ethyl-3-trifluoromethylpyrazole (XI). To a solution of 2.4 g (0.04 mol) of ethylhydrazine in 40–50 ml of anhydrous ether was slowly added dropwise 5.62 g (0.02 mol) of dibromovinyl ketone **I**. The reaction mixture self-heated, and ethylhydrazinium bromide precipitated. On completion of heat evolution the stirring continued for 1–2 h. The

precipitate of the ethylhydrazinium bromide was filtered off. From the filtrate on removing the solvents 2.72 g of pyrazole **XI** was isolated.

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