Tetrahedron. Vol. 24, pp. 1341 to 1356. Pergamon Press 1968. Printed in Great Britain

BIS(TRIFLUOROMETHYL)KETENE—VIII*†
REACTION WITH UNSATURATED COMPOUNDS

YU. A. CHEBURKOV, N. MUKHAMADALIEV and I. L. KNUNYANTS
Institute of Organo Element Compounds, Academy of Sciences of USSR, Moscow

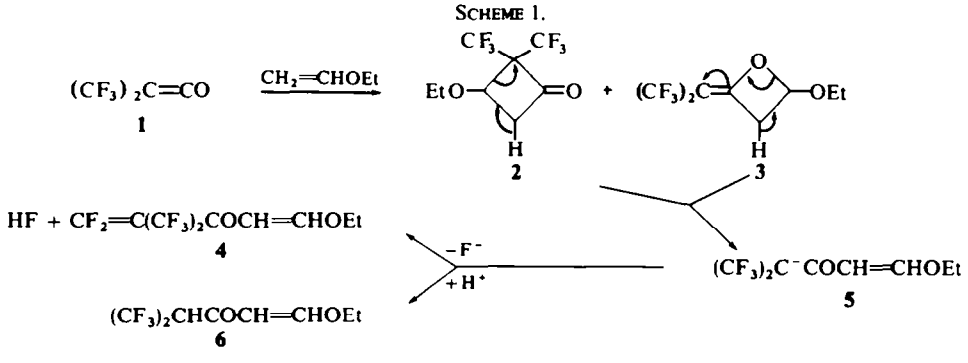
(*Received in UK* 3 *April* 1967; *accepted for publication* 13 *July* 1967)

Abstract—A study of the interaction of bis(trifluoromethyl)ketene (**1**) with vinyl ethyl ether, isobutene, butadiene, styrene and phenylacetylene reveals that in these reactions linear compounds (**6** and **11**) and cyclic ketones (**22** and **28**) are produced as well as dihydropyran (**18**). It was assumed that the pentenoic acids (**30** and **35**) formed in the hydrolysis of cyclobutenones (**28** and **32**) are produced as a result of the addition of water to the ketenes (**29** and **33**) in 1,4-position. Two new cases of a long-range spin–spin interaction of H and F atoms for the enol **13** and cyclobutanone (**31**) are described.

THE interaction of ketenes with olefins and dienes is a method for obtaining cyclobutane derivatives.[2] This reaction takes place in the absence of catalysts but often cannot be applied to simple aliphatic ketenes if there is a tendency to dimerize. Bis(trifluoromethyl)ketene does not dimerize on heating in the absence of catalysts[3] and therefore, its reactions with vinyl ethyl ether, isobutene, butadiene, styrene and phenylacetylene has been investigated.‡

Vinyl ethyl ether. Bis(trifluoromethyl)ketene (**1**) reacts violently with vinyl ethyl ether at −78° but polymerization of the ether and formation of tar can be prevented if the reaction is carried out in the presence of a solvent. Cyclobutanone (**2**) and oxetane (**3**), which are probably formed initially, could not be isolated in pure state owing to their isomerization into ethoxypentenone (**6**) (Scheme 1).

SCHEME 1.



Evidence in favour of the isomerization can be seen in the variation of the IR spectrum of the reactants in diethyl ether. After a 24-hr period, the IR spectrum of the solution kept at −10°, should be observed together with the absorption bands of ketone **6**, the absorption bands of the ketone **2** carbonyl group (CO in a 4-membered

* For the previous papers in this series, see reference 1.

† Translated by A. P. Kotlobye.

‡ For preliminary results, see Ref. 4.

ring at 1800 cm^{-1}), as well as those of double bonds: oxetane 3 (1647 cm^{-1}) and possibly ketone 4 (the CF_2=C group at 1746 cm^{-1}); whereas on distillation only a good yield of ketone 6 was obtained. The structure of 6 was based on analysis and its spectra. The isomerization of cyclobutanone 2 into ethoxypentenone 6 is not unexpected, since it is known[5] that 1-alkoxy and 1-alkylaminocyclobutan-3-ones obtained by cyclodimerization of ketenes with vinyl ethers or enamines are thermally unstable and readily isomerize into ketones of the type 6.

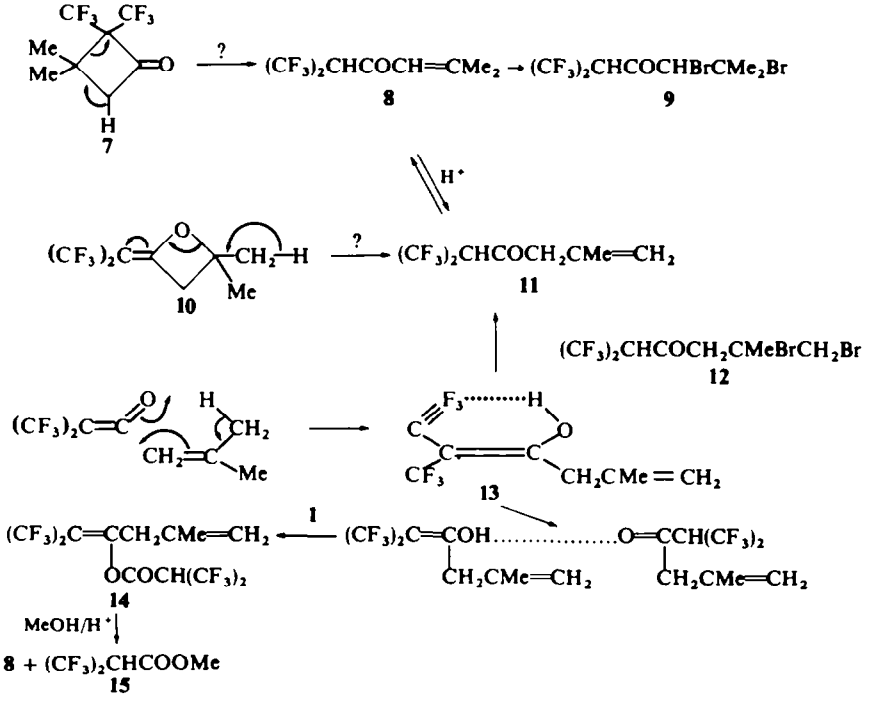
As regards the formation and the isomerization of oxetane 3, in the only one known case[6] of oxetane formation in reactions of ketenes with vinyl ethers the properties of the oxetane were not given, and therefore it is impossible to compare the isomerization of 3 into 6 with the literature data.

Isobutene. The reaction of ketenes with olefins, with a double bond and no adjacent activating groups was carried out under rigorous conditions without the use of catalysts. The product was independent of the nature of the olefins which may be cyclic[7–12] or linear [6, 11–13], and always is a cyclobutanone of the type (7) (Scheme 2). The reaction of bis(trifluoromethyl)ketene with isobutene at 0° without a solvent is slightly exothermic and yields hexenone (11) and a small amount of hexafluoroisobutyrylhydroxyhexadiene (14).

This reaction is an exception to the rule, because the unsaturated ketone 11, as shown later, is obtained directly from the ketene and the olefin and not via cyclobutanone 7 or oxetane 10.

During the isomerization of cyclobutanone, the formation of α,β-unsaturated hexenone (8) may be expected as a result of the transfer of the more acidic hydrogen atom from the methylene group adjacent to the carbonyl group (Scheme 2).

SCHEME 2.



An isomerization of ketone **8** into ketone **11** in the course of the reaction is excluded as the conjugated ketone **8** is more stable, and therefore, a reverse transition takes place—the isomerization of **11** into **8** in the presence of acids or triethylamine. The catalytic action of triethylamine in the isomerization of hexenone **11**, as in other similar isomerizations discussed in this work, can be explained by a mechanism which involves the separation of HF from the $(CF_3)_2CHCO$ group yielding triethylammonium fluoride. The latter acts as an acid. In other words, even in the case involving triethylamine as the catalyst, we apparently have the usual prototropic change (Eq. 1).

$$\mathbf{11} \xrightarrow{-H^+} (CF_3)_2CHCOCH_2C^+Me_2 \xrightarrow{-H^+} \mathbf{8} \quad (1)$$

The formation of the oxetane **10** as an intermediate in the reaction of bis(trifluoromethyl)ketene with isobutene is uncertain, no analogy for its isomerization to the hexenone **11** (Scheme 2) being known.[14]

Aside from these general and negative considerations concerning the mechanism of the formation of hexenone **11** in the reaction of bis(trifluoromethyl)ketene with isobutene, an attempt was made to solve the problem by PMR. The spectra of the substances placed in sealed ampoules were recorded periodically. In Fig. 1 the PMR spectra of the isobutene and bis(fluoromethyl)ketene mixture obtained after 8 hr at 0° (a) and after 4 hr (b) and 8 hr (c) at room temperature are shown.

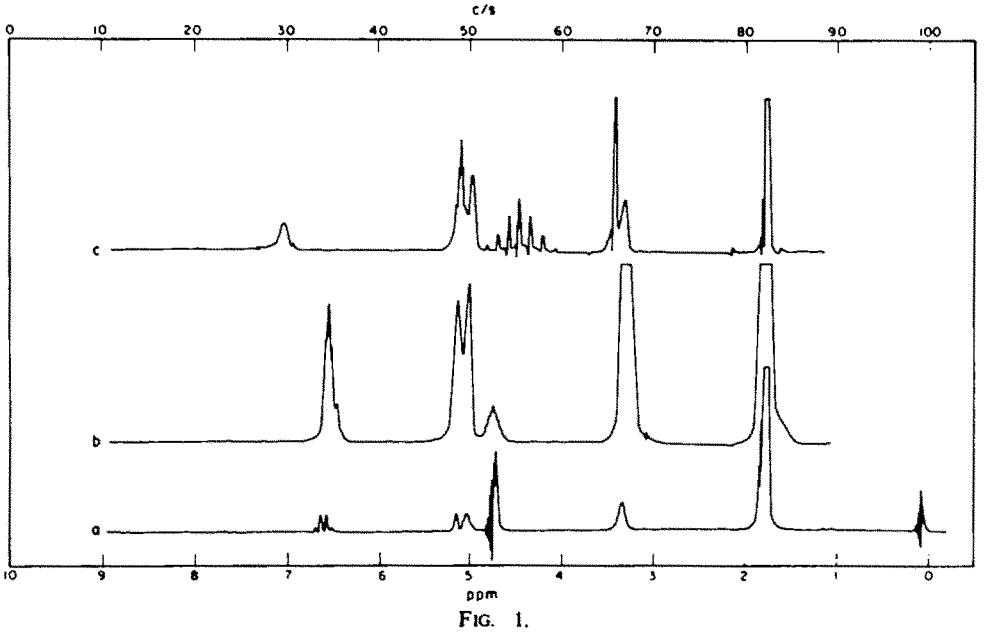


FIG. 1.

In the course of the reaction, isobutene (Me, 1·75 and CH_2, 4·72 δ, spectrum a) disappears, and in its place a compound characterized by signals 1·75, 3·34, 5·05, 5·15 and 6·55 δ (spectrum b) appears. Three of the signals (1·75, 5·05 and 5·15) are common for this compound and for the compound arising from it; the rest differentiate it from the final product of the reaction—ketone **11** (Me, 1·75 and CH_2, 3·40; septet CH, 4·46; CH_2, 4·97 and 5·10 δ, spectrum c).

The explanation of these changes is as follows: in this reaction, the enol of 2-methyl-6,6,6-trifluoro-5-trifluoromethyl-1-hexen-4-one (**13**) (Scheme 2) (CH_2, 3·34 and OH, 6·55, Fig. 1) first produced, slowly isomerizes into ketone **11**. The stabilization of the enol may first proceed through the formation of an intramolecular hydrogen bond between the hydrogen atom of the HO-group and the three fluorine atoms of one of the trifluoromethyl groups. This is evident from the splitting of the proton signal (see a, Fig. 1) into a quartet and from the fact that the quartet is located in a relatively high field (6·5 δ). This splitting with a constant of 3·3 c/s is evident in the early stages of the reaction, but is difficult to detect later. Whether the spin-spin interaction occurs through five bonds or through the hydrogen bond will be discussed later in this paper. In any case, the change in the concentration of the reactants, as the reaction proceeds, has no effect on the chemical shift of the hydroxyl proton—this is characteristic of an intramolecular hydrogen bond. As the reaction proceeds further the intramolecular bond gradually changes into the intermolecular hydrogen bond of enol **13** with the CO-group of the formed ketone **11** (scheme 2). This is clear from the down field shift of the proton signal of the HO-group (see c, Fig. 1) and the simultaneous disappearance of its fine structure. It is at this stage that the acylation of enol **13** by bis(trifluoromethyl)ketene takes place, yielding isobutyrylhydroxy-hexadiene **14** (ν_{max} 1675 cm^{-1} C=C and 1795 cm^{-1} CO; the PMR spectrum is practically the same as in the case of ketone **11**).

Thus regardless of the fact whether there is direct addition of isobutene to the CO-group of the ketene **1** or the reaction proceeds through the 6-membered cyclic transition state and is accompanied by allylic rearrangement as shown in Scheme 2, this can be considered as an example of a rare reaction of "C acylation" by ketenes.[15,16]

The structures of the products **8** and **11** were proved by analysis, the IR and PMR spectra, and by formation of the corresponding dibromoderivatives **9** and **12**. The hexadiene **14** on heating with methanol in the presence of sulphuric acid changes into ketone **8** and the hexafluoroisobutyric acid ester (**15**).

The PMR spectra of all the compounds except **12** are simple, and unequivocally prove the structures. The spectrum of **12** is more complex as the septet of the tertiary hydrogen atom overlaps the signals from the methylene protons of the CH_2Br-group, which in turn are split into a quartet of the AB type, as a result of non-equivalency. It is clear from the analysis of the rotational isomers of dibromohexanone **12** (Fig. 2) that the protons of the CH_2Br-group are non-equivalent, because the magnetic field in which they are located cannot be averaged even with fast rotation around the CBr—CBr bond.

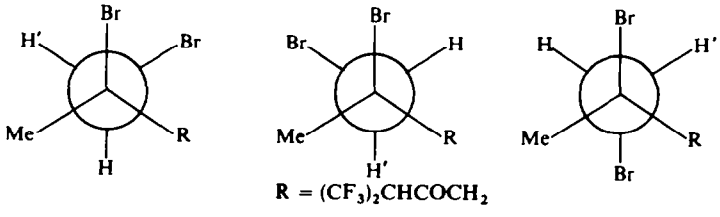
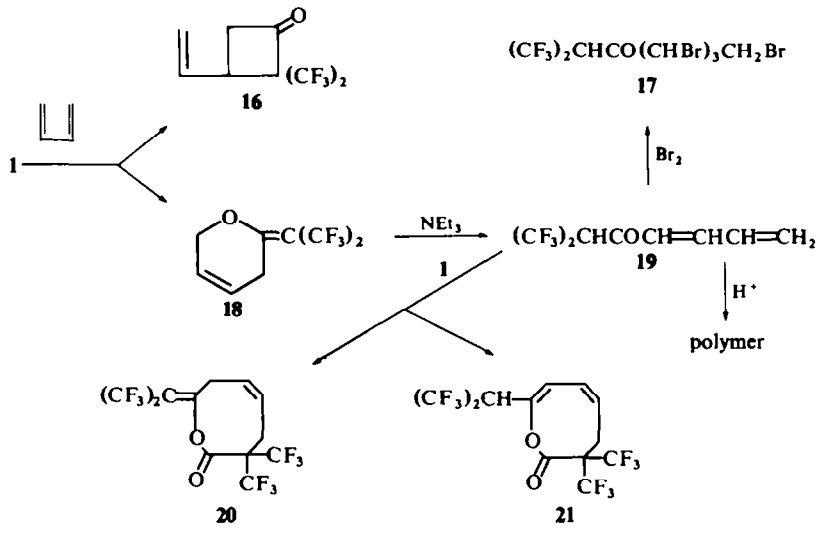


FIG. 2. Rotational isomers of 6,6,6-trifluoro-5-trifluoromethyl-2-methyl-1,2-dibromohexan-3-one **12**.

This phenomenon is also observed in other 1,2-dibromoderivatives.[17]

Butadiene. Dienes containing conjugated double bonds including butadiene[11, 12, 18, 19] and other linear dienes undergo cycloaddition with ketenes even more readily than simple olefins. The reaction always yields cyclobutanones of the type **16** (Scheme 3), i.e. products of 1,2-cycloaddition. The 1,4-cycloaddition of ketenes to linear dienes[8, 20] was shown[18] to be incorrect with no experimental confirmation. Recently however, it was found[11] that 1,4-cycloaddition does take place with certain ketenes but the C=O and not C=C group of the ketene reacts yielding dihydropyrans of the type **18** (Scheme 3).

SCHEME 3.



This exceptional case was observed in the reaction of butadiene with bis(trifluoromethyl)ketene. The dihydropyrane **18** obtained is unstable and upon storage gradually or rapidly in the presence of catalytic amounts of triethylamine isomerizes to the conjugated unsaturated ketone **19**, which readily polymerizes.

In the NMR H^1 and F^{19} spectra of dihydropyran **18**, three isometric multiplets from groups CCH_2, OCH_2, and CH=CH appear as well as two quartets of trifluoromethyl groups; whereas the PMR spectrum of the ketone **19** contains a complex multiplet caused by unsaturated protons in the 5–8 δ region and a septet caused by the presence of the tertiary hydrogen atom in the hexafluoroisopropyl group, unequivocally proving the rearrangement of dihydropyran **18** into ketone **19**. The ketone **19** is also converted into tetrabromoketone (**17**).

In the reaction between bis(trifluoromethyl)ketene and butadiene, in addition to dihydropyran **18**, a small amount of a substance corresponding in composition to an adduct of two moles of the ketene and one mole of the diene is formed. The adduct can also be synthesized in good yield on heating of equivalent amounts of bis(trifluoromethyl)ketene and ketone **19**. This substance, in the basis of the method of synthesis and its IR spectrum, may be considered as an unsaturated lactone **20** or **21** (Scheme 3). The IR spectrum of the lactone contains the absorption bands of vinyl ester C=COC=O-group at 1682 and 1718 cm^{-1}. The PMR spectrum, though complex, indicates the absence of a vinyl group $CH=CH_2$. The choice in favour of

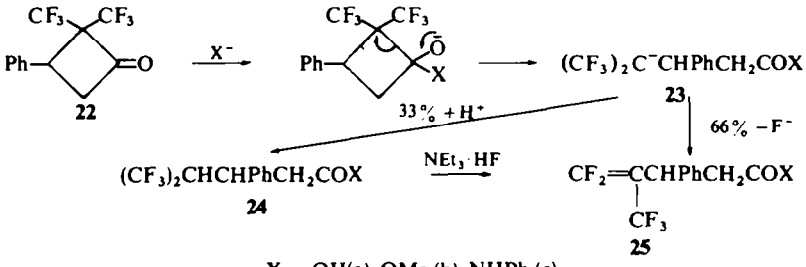
2,2-bis(trifluoromethyl)-7-(2'-H-hexafluoroisopropyl)-4,6-heptadien-7-olide (**21**) was made on the basis of its NMR F^{19} spectrum, which consists of two quartets of non-equivalent CF_3 groups in the 8-membered cycle (6 F) and a doublet $(CF_3)_2CH$ group (6 F). In order to prove that the doublet is due to spin-spin coupling in the $(CF_3)_2CH$-group, the spectrum was repeated with two different instruments (20 and 60 Mc).

It follows that the lactone **21** is formed as a result of 1,6-cycloaddition of bis-(trifluoromethyl)ketene to unsaturated ketone **19**. Such reactions of ketenes with carbonyl compounds are well known.[16,21]

Styrene. Styrene undergoes cyclodimerization with ketene **1** yielding cyclobutanone **22** (Scheme 4). In the IR spectrum, the absorption frequency of the carbonyl group lies at 1820 cm^{-1} and is somewhat higher as compared with other cyclobutanones.[22] This may be due to the effect of the fluorine atom. The behaviour of bis(trifluoromethyl)ketene does not differ in this reaction from that of dimethyl-[7,12] and diphenylketene[8,23–25] if some errors in the determination of the structure of the product, obtained from diphenylketene[8,24] are taken into account; the errors were later corrected.[24,25]

Up to this time cyclobutanones containing *gem*-bis(trifluoromethyl) groups as substituents were unknown. It has been found by the present authors that the cyclobutanones exhibit certain peculiarities during reactions accompanied by the opening of the 4-membered cycle. First, such reactions for cyclobutanone **22** proceed readily at room temperature and in the absence of a catalyst. Second, two series of the products are formed: saturated **24** and unsaturated **25** acids, the latter being predominant. In the presence of water, methanol, and aniline ketone **22** yields mixtures of pentanoic **24a** and pentenoic **25a** acids or their derivatives (Scheme 4).

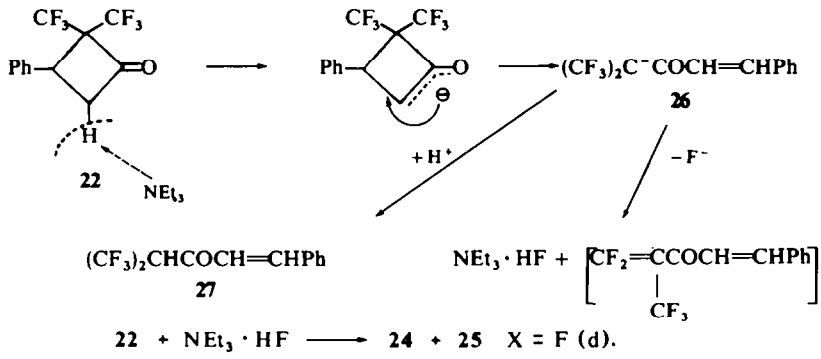
SCHEME 4.



X = OH(a), OMe (b), NHPh (c).

In these reactions the ring opening takes place along the bond adjacent to the carbonyl group. The opening of the ring in cyclobutanone **22** proceeds differently in the presence of triethylamine (Scheme 5), the product being hexenone (**27**) which is an isomer of the initial compound—cyclobutanone **22**. The intermediate anione **26**, which can be stabilized in two ways, is a potential source of triethylammonium fluoride. The latter converts the starting cyclobutanone **22** into the mixture of acyl fluorides **24d** and **25d**.

SCHEME 5.



The mixture **24** and **25** cannot be separated by the usual methods, since these substances have very close constants. Even GLC analysis shows the presence of only one component. However, data from the elemental analysis and the spectra prove the presence of two compounds. In the IR spectrum of the mixture the absorption of the CF_2=C group always lies near 1750 cm^{-1}, so that in the acid **25a** and anilide **25c** the frequency of carbonyl group is smaller than the frequency of the double bond, whereas in the ester these absorption bands coincide. A typical PMR spectrum of the mixture is shown in Fig. 3.

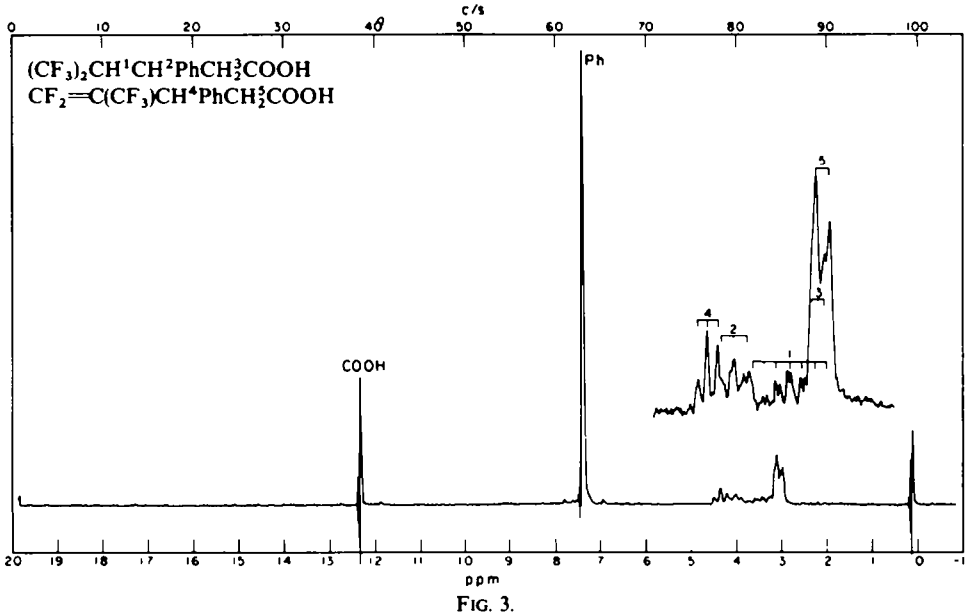


FIG. 3.

The ratio **24** to **25** given in Scheme 4 was obtained only once, for mixtures of methyl esters **24b** and **25b** by the integration of separate signals from two different MeO groups. We were unable to separate these mixtures into components, but the saturated 3-phenyl-5,5,5-trifluoro-4-trifluoromethylpentanoic acid **24a**, its ester, anilide and acyl fluoride were synthesized by other methods. The compounds **24a**

and **24b** were obtained by means of catalytic hydrogenation (Eq. 2) of the corresponding unsaturated derivatives **30**, which were synthesized from cyclobutenone **28** (Scheme 6); the synthesis is described in detail in the section, in which the reaction of bis(trifluoromethyl)ketene with phenylacetylene is considered (see below).

$$(30)\mathbf{a,b} \xrightarrow{H_2/Pd} \mathbf{24,a,b} \qquad (2)$$

The anilide **24c** was obtained from the acid **24a** by the subsequent action of PCl_5 and aniline. Finally, the mixture of acyl fluorides **24d** and **25d** was converted into pure acyl fluoride **24d** by treating the mixture with triethylammonium fluoride (Scheme 4; cf. Ref. 26).

A feature of the NMR F^{19} spectrum of the derivatives of the pentanoic acid **24** is that signals from trifluoromethyl groups are quintets. The trifluoromethyl groups in **24** are nonequivalent because they are in the vicinity of an asymmetric centre of the molecule (cf. Fig. 2) and must be split by one another into a quartet. The observed quintets are in reality doublets of quartets owing to an additional interaction with the tertiary hydrogen atom with approximately the same constants ($J_{FF} = J_{HF}$).

The formation of the two series of derivatives in the ring-opening reactions of 4-membered cyclic ketones with *gem*-bis(trifluoromethyl) groups may be by two parallel processes independent of one another and this formation can be considered as one of the characteristics of the compounds.

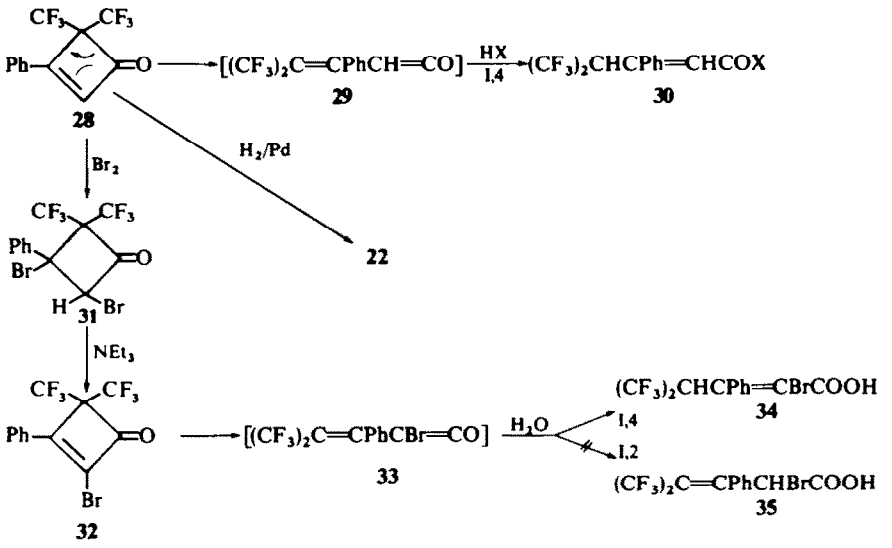
Phenylacetylene. The reaction of bis(trifluoromethyl)ketene with phenylacetylene yields 2,2-bis(trifluoromethyl)-3-phenyl-3-cyclobutenone **28** (Scheme 6). Up to now it was impossible to carry out a direct synthesis of cyclobutenones from ketenes and acetylene derivatives. Though probably not the best examples were investigated—too reactive unsubstituted ketene[27] and diphenylketene.[28–30] After correcting[30] the mistakes made in the previous works[28,29] it became evident that in the reaction with diphenylketene one of the benzene nuclei in the ketene participated in the reaction, thus no cyclobutenones were formed. However, phenylcyclobutenones could be synthesized by an indirect method, i.e., by the hydrolysis of halogenated cyclobutenes.[31–34] These latter compounds are readily obtained by cyclodimerization of phenylacetylene and styrene with fluoroolefins.[2]

The structure of cyclobutenone **28** is confirmed by catalytic hydrogenation which converts it into saturated ketone **22** (Scheme 6). It is difficult to select a solvent for hydrogenation; water and alcohol are not suitable because they react with the starting material and with ketones produced in the reaction, forming acids and esters of the type **24**, **25** and **30**. We limited ourselves to the identification of the saturated ketone **22** in the reaction mixture with the GLC technique and IR spectroscopy (through the absorption band of the carbonyl group of cyclobutanone **22** at 1820 cm^{-1}).

Water, methanol, dimethylamine and aniline transform the *gem*-bis(trifluoromethyl)cyclobutenone **28** into 3-phenyl-5,5,5-trifluoro-4-trifluoromethyl-2-pentenoic acid **30a**, its ester and amides (Scheme 6).

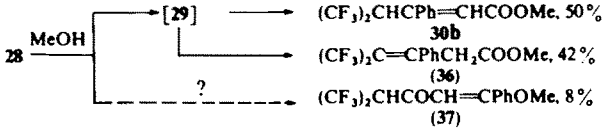
When cyclobutenone **28** reacts with water or dimethylamine, only one substance is formed (acid **30a** or amide **30d**) while the reaction with methanol is more complicated. An examination of IR and NMR spectra of the crude reaction mixture shows that the mixture consists of three components two of which are the esters **30b** and **36**, Eq. 3. It is possible that cyclobutenone **28** initially isomerizes into unsaturated

SCHEME 6.



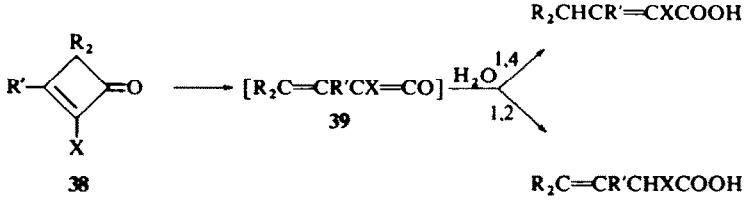
X = OH (a); OMe (b); NHPh (c); NMe_2 (d).

ketene **29**, which later adds methanol across the 1,4 or 1,2 position (cf. Eq. 4), giving esters **30b** or **36** respectively. The third component of the crude mixture may be methoxyphenylpentenone (**37**), Eq. 3. We could not prove the structure of the substance, because we could not establish the character of the splitting of its PMR signal at ~4 δ. The septet $(CF_3)_2CHCO$ group at 4·0 δ is the only signal which distinguishes the ketone **37** from isomeric esters **30b** and **36**.



(3)

gem-Bis(trifluoromethyl)cyclobutenone **28** is hydrolyzed in acetone solution to pentenoic acid **30a** (Scheme 6) without a catalyst at room temperature. The same acid is obtained if the hydrolysis is carried out at low temperature in the presence of 10%—HCl or acetic acid under conditions, described by Roberts *et al.*[33] for 2,2-dichloro-3-phenyl-3-cyclobutenone (**38**, R = Cl, R′ = Ph, X = H). These authors have postulated the following mechanism of acidic hydrolysis (Eq. 4). First, cyclobutenone **38** isomerizes to vinyl ketene **39**, which adds water in either the 1,2- or 1,4-position, depending on the degree of coplanarity of its double bonds.



(4)

The breaking of coplanarity and the addition in the 1,2-position takes place when the substituents R, R', and X in ketene **39** are large (for instance, when R[33] or X[32–35] are chlorine atoms, and R' = Ph).

If this version is correct, then the results of acidic hydrolysis of *gem*-bis(trifluoromethyl)cyclobutenone **28** are remarkable in that the CF_3-groups, which are larger[36] than chlorine atoms, do not break the coplanarity (or conjugation) in the ketene **29** (Scheme 6) and the addition of water to the ketene occurs at the 1,4-position. Even if in ketene **29** a certain amount of disturbance of the total coplanarity of the system occurs (the trifluoromethyl group removes the Ph from the conjugation with the double bond), one could consider that this effect is small and therefore does not prevent the 1,4-addition. There is only one case[33] of conjugation being broken by chlorine in the analogous ketene **39** (R, R', X = Cl, Ph, H) (Eq. 4). This case may be an exception. In order to eliminate two double bonds in ketene **29**, it is necessary to substitute a hydrogen atom for halogen. As it is known in the analogous ketene **39** (X = Cl), the breaking of coplanarity always results in 1,2-addition.[32–35]

The required cyclobutenone **32** was obtained from cyclobutenone **28** by means of bromination followed by dehydrobromination (Scheme 6). Hydrolysis of **32** was investigated, and it was shown that bromocyclobutenone **32** is more stable in the presence of water than cyclobutenone **28**—it is not hydrolyzed by aqueous acetone at room temperature, but, after boiling in acetic acid and then in water it gives 2-bromo-3-phenyl-5,5,5-trifluoro-4-trifluoromethyl-2-pentenoic acid (**34**). In other words, in spite of the presence of steric hindrance in vinylbromoketene **33** (Scheme 6), the addition of water takes place in the 1,4-position.

It is therefore not possible to predict the products of acidic hydrolysis of 4-membered cyclic ketones in the case of *gem*-bis(trifluoromethyl) derivatives.

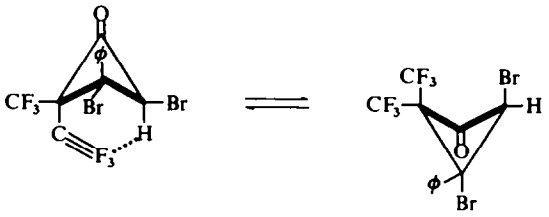
In the PMR spectrum of ketone **31** (Scheme 6) the signal of the hydrogen atom in the ring is split into a quartet with a constant ~2 c/s, owing to the long-range spin-spin interaction with three fluorine atoms of one CF_3-group. Takahashi *et al.*[37] have proved that such interaction takes place between substituents that are in *cis*-position in respect to each other (**31a**, Fig. 4), and it is generally assumed that the interaction takes place directly through the space of the molecule.

Generally speaking, the often used phrase "through the space" is not unambiguous. When we speak about the long-range spin–spin splitting of identical atoms (HH[38] or FF[39]) through the space, we mean the absence of a direct chemical bond between the atoms.

But in the case of the hydrogen and fluorine atoms, it is often possible to assume the formation of a hydrogen bond, in which case the phrase "through the space" means in reality the probability of spin–spin interaction through the hydrogen bond. Such a mechanism of a long-range interaction should not be disregarded, and perhaps this phenomenon is observed in the case of ketone **31** or enol **13**, as well as in other known cases.[40] The 4-membered ring of ketone **31** either must be firmly bent (Fig. 6) (concerning conformations of cyclobutanes, see review[41] by Lambert and Roberts), or its inversion must proceed at such a rate, that the formation of the hydrogen bond through the space of the molecule could occur during the time required for the formation of the spectrum.

In the present work the reactions of bis(trifluoromethyl)ketene with unsaturated compounds illustrate the marked electrophilic affinity of this ketene. All the reactions

take place under milder conditions than required for similar reactions of other ketenes and yield a series of new and interesting fluoroorganic compounds.



31a 31b

FIG. 1. Conformations of cyclobutanone 31.

EXPERIMENTAL

M.ps are uncorrected. The IR spectra were taken in a UR-10 spectrophotometer. The NMR spectra were recorded on Hitachi H 6013 NMR instrument for CCl_4 solns at 35° with hexamethyldisiloxane or $C_2F_2Cl_4$ as an internal standard; chemical shifts are given in δ ppm to TMS or τ ppm to CCl_3F. The chemical shifts of hexamethyldisiloxane and $C_2F_4Cl_2$ were taken to be 0·05 δ and 69·0 τ respectively from TMS and CCl_3F. The UV spectra were taken in a SF-4A spectrophotometer. Polyesters and thiols were used as the stationary phase in the GLC analysis.

Reaction of ketene **1** *with vinyl ethyl ether*

A mixture of **1** (5 g) and vinyl ethyl ether (2·2 g) in Et_2O was kept for 36 hr at 20°, then for 1 hr at 100°, followed by distillation yielding 4·2 g (58% yield) of **6** m.p. 20–24°, b.p. 40–41°/3 mm; ν_{max} 1595 and 1615 (C=C), 1680 and 1695 cm^{-1} (CO); PMR: 4·12 (septet CH, J = 7·0 c/s), 5·80 and 7·75 (AB quartet CH=CH, J = 12 c/s), 4·04 (quartet CH_2), 1·30 (triplet CH_3). (Found: C, 38·1; H, 3·25; F, 45·4. $C_8H_8F_6O_2$ requires: C, 38·4; H, 3·20; F, 45·6%.)

Reaction of ketene **1** *with isobutene*

A mixture of **1** and i-C_4H_8 (2·58 g) was kept in a sealed ampoule for 24 hr at 20°, followed by distillation yielding 8·7 g of **11** and 1·1 g of **14**. B.p. of **11** 45°/20 mm, n_D^{20} 1·3515; λ_{max} pet. ether 296 mμ, log ε_{max} 1·93; ν_{max} 1660 (C=C), 1748 (CO), 3096 cm^{-1} (=CH_2); PMR: 4·46 (septet CH, J = 8·0 c/s), 3·40 (CH_2), 1·75 (doublet CH_3, J = 1·3 c/s), 4·97 and 5·10 (=CH_2); NMR F^{19}: 67·2 (doublet CF_3, J = 8·0 c/s). (Found: C, 40·9; H, 3·19; F, 48·9. $C_8H_8F_6O$ requires: C, 41·0; H, 3·42; F, 48·7%.)

B.p. of **14** 78°/20 mm, n_D^{20} 1·3488; ν_{max} 1675 (C=C), 1795 (CO), 3080 cm^{-1} (=CH_2); PMR: 4·10 (septet CH, J = 7·5 c/s), 3·38 (CH_2), 1·70 (CH_3), 4·7 and 4·9 (=CH_2). (Found: C, 34·9; H, 2·04; F, 55·0. $C_{12}H_8F_{12}O_2$ requires: C, 34·9; H, 1·94; F, 55·4%.)

The diene **14** was heated for 15 min in MeOH containing a drop of H_2SO_4, followed by washing with water and drying. The product was identified (GLC) as **8** and a known[42] methyl ester **15**.

1,2-*Dibromo*-6,6,6-*trifluoro*-5-*trifluoromethylhexan*-4-*one* (**12**)

To **11** (5 g) at 5° Br_2(3·5 g) was added and the mixture distilled yielding 6·3 g (75% yield) of **12**, m.p. 7–8°, b.p. 106–108°/16 mm, n_D^{20} 1·4291, ν_{max} 1743 cm^{-1} (CO); PMR: 4·22 (septet CH, J = 6·0 c/s), 3·54 (CH_2), 2·00 (CH_3), 3·90 and 4·30 (AB quartet CH_2Br, J = 10 c/s); NMR F^{19}: 65·2 (doublet CF_3, y = 8·0 c/s). (Found: C, 24·4; H, 1·99; Br. 40·4; $C_8H_8Br_2F_6O$ requires: C, 24·4; H, 2·03; Br, 40·6.%.)

Isomerization of ketone **11**

The mixture of **11** (6·4 g) and H_2SO_4 (5 drops) was heated at 100° for 150 min and distilled yielding 6·0 g of **8**, b.p. 55–56°/20 mm; λ_{max} pet. ether (log ε_{max}): 244 (4·22), 324 mμ (1·79); ν_{max} 1612 (C=C), 1695 cm^{-1} (CO); PMR: 4·35 (septet CH, J = 8·0 c/s), 6·35 (=CH), 1·98 and 2·25 (CH_3). (Found: C, 40·8; H, 3·40; F, 49·5. $C_8H_8F_6O$ requires: C, 41·0; H, 3·42; F, 48·7%.)

2,3-Dibromo-6,6,6-trifluoro-5-trifluoromethyl-2-methylhexan-4-one (**9**)

To ketone **8** (0·88 g) at 0° 0·6 g dry Br_2 was added and the crystalline solid obtained was recrystallized from 80% EtOH/H_2O yielding 1·2 g of **9**, m.p. 53–54°; $\lambda_{max}^{heptane}$ 305 mμ, log ε_{max} 1·86; ν_{max} 1753 cm^{-1} (CO); PMR: 4·50 (septet CH, J = 7·0 c/s), 4·87 (CHBr), 2·00 (CH_3); NMR F^{19}: 65·0 and 64·3 (two quartets CF_3, J = 8·8 c/s). (Found: C, 24·2; H, 2·06; Br, 40·1. $C_8H_8Br_2F_6O$ requires: C, 24·4; H, 2·03; Br, 40·6%.)

Reaction of ketene **1** *with butadiene*

A mixture of **1** (10·5 g), butadiene (3·2 g) and hydroquinone (0·01 g) was heated in a sealed ampoule at 70° for 35 hr, and then distilled yielding 12·5 g (90% yield) of **18**, b.p. 76–78°/15 mm, n_D^{20} 1·3965; ν_{max} 1628 cm^{-1} (C=C); PMR: 3·25 (multiplet CCH_2), 4·74 (multiplet OCH_2), 6·10 (multiplet CH=CH); NMR F^{19}: 56·5 and 59·8 (quartets CF_3, J = 9·9 c/s). (Found: C, 41·7; H, 2·64. $C_8H_6F_6O$ requires: C, 41·4; H, 2·58%.)

The crude product consisted of 92% of **18** and 8% of **21** (GLC).

Isomerization of dihydropyran **18**

Dihydropyran **18** (5 g) was distilled in the presence of two drops NEt_3 yielding a tar and 2·9 g (56%) of **19**, b.p. 44–46°/16 mm, n_D^{20} 1·3948; ν_{max} 1580 and 1620 (C=C), 1700 and 1710 (CO), 3092 cm^{-1} (=CH_2); PMR: 4·13 (septet CH, J = 8·4 c/s), 5–8 (multiplet CH=CHCH=CH_2); NMR F^{19}: 65·6 (doublet CF_3, J = 7·7 c/s). (Found: C, 41·0; H, 2·59; F, 50·6. $C_8H_6F_6O$ requires: C, 41·4; H, 2·58; F, 49·2%.)

1,2,3,4-Tetrabromo-7,7,7-trifluoro-6-trifluoromethylheptan-5-one (**17**)

Ketone **19** was mixed with Br_2 at 0° yielding 70% of **17**, m.p. 99–100° (from heptane); ν_{max} 1757 cm^{-1} (CO); PMR: 4·38 (septet CH, J = 7·5 c/s), 3–5 (multiplet CHBr and CH_2Br); NMR F^{19}: 63·6 and 65·2 (two double quartets CF_3, J = 8·8 and 7·7 c/s). (Found: C, 17·8; H, 1·20; Br, 58·0. $C_8H_6Br_4F_6O$ requires: C, 17·4; H, 1·09; Br, 58·0%.)

2,2-Bis(trifluoromethyl)-7-(2'-H-hexafluoroisopropyl)-4,6-heptadien-7-olide (**21**)

Ketene **1** (2·13 g) and **19** (2·82 g) were heated in a sealed ampoule at 100° for 12 hr, and then distilled. There was 4·02 g (82% yield) of **21**, m.p. 16–17°, b.p. 113–115°/16 mm, n_D^{20} 1·3758; $\lambda_{max}^{heptane}$ (log ε_{max}): residual absorption after 220, 313 (1·7), 325 mμ (1·7); ν_{max} shoulder 1663 (CH=CH), 1685 (C=C), 1820 cm^{-1} (CO); PMR: 3·3–5·5 (complex multiplet). NMR F^{19}: 66·1 (broad quartet CF_3, J = 8·0 c/s), 68·1 (doublet, CF_3, J = 8·8 c/s at 56 Mc and 8·0 c/s at 21 Mc. Each component of the doublet split by one CF_3 in 8-membered ring into quartet, J = 1·6 c/s), 70·9 (quartet CF_3, J = 8·0 c/s). (Found: C, 34·7; H, 1·62; F, 55·0. $C_{12}H_6H_{12}O_2$ requires: C, 35·1; H, 1·46; F, 55·6%.)

2,2-Bis(trifluoromethyl)-3-phenylcyclobutanone (**22**)

Ketene **1** (10·7 g), styrene (6·3 g), and hydroquinone (0·01 g) were heated in a sealed ampoule (100°, 10 hr) and distilled, yielding Polystyrene and 13·7 g (80% yield) of **22**, m.p. 9–10°, b.p. 94°/7 mm, n_D^{20} 1·4428; λ_{max} pet. ether (log ε_{max}): 242 (2·88), 247 (2·89), 290 mμ (1·61); ν_{max} 1500, 1600, 3042 (Ph); 1820 cm^{-1} (CO); PMR: 3–4·5 (ABC multiplet $CHCH_2$, 9 lines), 7·22 (Ph); NMR F^{19}: 65·0 and 69·6 (two quartets CF_3, J = 8·5 c/s). (Found: C, 51·0; H, 2·84; F, 40·0. $C_{12}H_8F_6O$ requires: C, 51·1; H, 2·84; F, 40·4%.)

Ring opening of ketone **22**

With water. A mixture of **22** (10·9 g) and H_2O (2 ml) was homogenized by the addition of acetone and kept at 20° for 12 hr. The solvent was evaporated and the residue was diluted with Et_2O and distilled after drying yielding 6·5 g of a mixture of acids **24a** and **25a**, b.p. 133–135°/4 mm, n_D^{20} 1·4528; ν_{max} 1505, 1610 (Ph); 1721 (CO); 1740 (CF_2=C); broad 2400–3500 cm^{-1} (OH); PMR (Fig. 3). NMR F^{19} **24a**: 63·6 and 66·3 (two double quartets CF_3, J = 9·7 and 9·7 c/s). NMR F^{19} of **25a**: 60·4 (double doublet CF_3, J = 22 and 11 c/s), 75·5 (double quartet CF=, J = 22 and 22 c/s), 79·3 (double quartet CF=, J = 22 and 11 c/s). (Found: C, 49·7; H, 3·25; F, 36·1. $C_{12}H_{10}F_6O_2$ requires: C, 48·0; H, 3·33; F, 38·0. $C_{12}H_9F_5O_2$ requires: C, 51·5; H, 3·21; F, 33·9%.)

With methanol. Ketone **22** (22·5 g) in 30 ml MeOH was kept for 12 hr at 20° and diluted with H_2O; the oil was extracted with Et_2O, dried and distilled yielding 21·7 g of a mixture of esters **24b** and **25b** in the ratio of 1:2 (by integration of OMe signals in PMR), b.p. 120°/15 mm, n_D^{20} 1·4442; ν_{max} 1500, 1590, 1610, 3033 (Ph); 1750 cm^{-1} (CO and CF_2=C); PMR of **24b**: CF_3CH is masked by OMe, 4·2 (double triplet PhCH, J = 7·3 and 3·4 c/s), 2·97 (doublet CH_2), 3·43 (CH_3), 7·30 (Ph). NMR F^{19} of **24b**: 64·3 and 66·2 (two double quartets CF_3, J = 9·7 and 9·7 c/s). PMR of **25b**: 4·36 (triplet CH, J = 7·7 c/s), 2·90 (doublet

CH_2), 3·53 (CH_3), 7·30 (Ph). NMR F^{19} of **25b**: 60·8 (double doublet CF_3, J = 21 and 10 c/s), 76·6 (double quartet CF=, J = 21 and 21 c/s), 79·8 (double quartet CF=, J = 21 and 10 c/s). (Found: C, 52·1; H, 4·10; F, 33·5. $C_{13}H_{12}F_6O_2$ requires: C, 49·7; H, 3·82; F, 36·3. $C_{13}H_{11}F_5O_2$ requires: C, 53·1; H, 3·74; F, 32·3%.)

With aniline. Ketone **22** (2·1 g) and aniline (1·1 g) in 20 ml Et_2O was kept overnight, washed with HCl/H_2O, dried and the solvent evaporated. Recrystallization of the residue from heptane yielded 2·0 g of a mixture anilides **24c** and **25c**, m.p. 82–90°; ν_{max} 1507, 1545, 1555, 1607, 3045 (Ph); 1667 (CO); 1750 (CF_2=C); 3210, 3290 cm^{-1} (NH). (Found: C, 59·4; H, 4·02; F, 28·7. $C_{18}H_{15}F_6ON$: C, 57·6; H, 4·00; F, 30·4. $C_{18}H_{14}F_5ON$ requires: C, 60·8; H, 3·95; F, 26·7%.)

With triethylamine. Ketone **22** (15·2 g) and NEt_3 (0·5 g), dried over Na-wire, were heated for 5 hr at 120° and distilled through a fractionating column yielding a mixture of 7·3 g of acyl fluorides **24d** and **25d**, b.p. 69–70°/3 mm, n_D^{20} 1·4358; ν_{max} 1495, 1587, 1600, 1628, 3033 (Ph); 1735 (CF_2=C); 1800; 1840 cm^{-1} (CO). PMR of **24d**: 3·40 (double septet CF_3CH, J = 8·5 and 3·4 c/s), 3·91 (double triplet PhCH, J = 3·4 and 7·7 c/s), 3·17 (doublet CH_2, J = 7·7 c/s), 7·28 (Ph). PMR of **25d**: 4·20 (triplet CH, J = 7·8 c/s), 3·10 (doublet CH_2, J = 7·8 c/s), 7·28 (Ph). (Found: C, 50·2; H, 2·81; F, 41·3. $C_{12}H_9F_7O$ requires: C, 47·7; H, 2·97; F, 44·1. $C_{12}H_8F_6O$ requires: C, 51·1; H, 2·84; F, 40·4%.)

The residue after being recrystallized from heptane yielded 2·4 g (16%) of **27**, m.p. 57°. b.p. 127–130°/14 mm; ν_{max} 1500, 1575, 3035 (Ph); 1607 (Ph and C=C); 1693 cm^{-1} (CO); PMR: 4·23 (septet CH, J = 7·7 c/s), 6·88 and 7·72 (AB quartet CH=CH, J = 17·1 c/s), 7·45 (multiplet Ph); NMR F^{19}: 65·1 (doublet CF_3, J = 7·2 c/s). (Found: C, 50·8; H, 2·84; F, 40·1. $C_{12}H_8F_6O$ requires: C, 51·1; H, 2·84; F, 40·4%.)

2,2-*Bis(trifluoromethyl)*-3-*phenyl*-3-*cyclobutenone* (**28**)

Ketene **1** (7·0 g) and phenylacetylene (4·0 g) were heated for 8 hr at 100° in a sealed ampoule and then distilled yielding 7·2 g (80% yield) of **28**, m.p. 24–25°, b.p. 125–127°/15 mm; λ_{max} pet. ether (log ε_{max}): 222 (3·69) and 285 mμ (3·99); ν_{max} 1495, 1562, 1590, 1605 (Ph); 1705 vw; 1720 w; 1760 sh; 1795 cm^{-1} (CO); PMR: 6·95 (CH), 7·52 (multiplet Ph); NMR F^{19}: 66·5 (CF_3). (Found: C, 50·9; H, 2·19; F, 41·7. $C_{12}H_6F_6O$ requires: C, 51·4; H, 2·14; F, 40·7%.)

Ring opening of ketone **28**

With water. Cyclobutenone **28** (20·7 g) and 1 ml H_2O after homogenization by adding acetone was kept at 20° for 12 hr. The solvent was evaporated and the residue reprecipitated from $NaHCO_3/H_2O$, dried and recrystallized from heptane yielding 2·7 g (94% yield) of **30a**, m.p. 124°; ν_{max} 1580, 1595, 1607 (Pj); 1635 (C=C); 1710 (CO); broad 2800–3300 cm^{-1} (OH); PMR: 6·30 (septet CH, J = 7·7 c/s), 6·38 (=CH), 7·46 (Ph), 12·0 (OH). (Found: C, 48·3; H, 2·75; F, 38·6. $C_{12}H_8F_6O_2$ requires: C, 48·4; H, 2·68; F, 38·5%.)

With methanol. Cyclobutenone **28** (30 g) in 10 ml MeOH was kept at 20° for 48 hr, diluted with H_2O, extracted with Et_2O, dried and distilled yielding 30·8 g of light yellow liquid, b.p. 115–116°/15 mm; ν_{max} 1647 (C=C **30b**); 1665 (C=C **36**); 1725 (CO **30b**); 1752 cm^{-1} (CO **36**); PMR: 7·31 (common Ph); 6·59 (septet $(CF_3)_2$ CHCPh, J = 8·6 c/s); 3·9 (possibly septet $(CF_3)_2CHCO$); 6·40 and 6·22 (CH=); 3·75, 3·55, 3·50 (singlets OMe and $COCH_2$); NMR F^{19} consists of four signals with intensities 21 : 21 : 50 : 8 and chemical shifts being respectively: 55·3 and 57·1 (two quartets $(CF_3)_2C$= **36**, J = 9·0 c/s); 61·2 and 64·5 (two doublets $(CF_3)_2CH$ **30b** and possibly **37**, J = 8·9 c/s).

After passing the mixture through a fractionating column containing metal packing, 17·4 g (51% yield) of **30b**, b.p. 74°/1 mm, n_D^{20} 1·4480 was obtained; PMR: 7·31 (Ph); 6·59 (septet CH); 6·22 (CH=); 3·75 (OMe); NMR F^{19}: 61·2 (doublet CF_3). (Found: C, 50·0; H, 3·34; F, 36·6. $C_{13}H_{10}F_6O_2$ requires: C, 50·0; H, 3·20; F, 36·5%.)

With aniline. Cyclobutenone **28** (1·2 g) and aniline (0·63 g) in 20 ml Et_2O were kept at 20° for 24 hr. The ether was evaporated and the residue treated with HCl/H_2O, dried and recrystallized from heptane yielding 0·4 g (25%) of **30c**, m.p. 138·5°; ν_{max} 1505, 1555, 1610 (Ph); 1645 (C=C); 1660 (CO); 3310 cm^{-1} (NH); NMR F^{19}: 62·9 (doublet CF_3, J = 8·1 c/s). (Found: C, 57·6; H, 3·44; N, 3·67. $C_{18}H_{13}F_6ON$ requires: C, 57·9; H, 3·49; N, 3·75%.)

With dimethylamine. Cyclobutenone **28** (7·7 g) and Me_2NH (1·3 g) were kept in 50 ml Et_2O for 24 hr. The ether was evaporated, the residue treated with HCl/H_2O, diluted with C_6H_6, boiled with activated charcoal until discoloured, followed by filtration and evaporation of C_6H_6. The residue was recrystallized from heptane yielding 7·1 g (79% yield) of **30d**, m.p. 45°. ν_{max} 1500, 1605, 1643 cm^{-1}; PMR: 6·49 (septet CH, J = 8·7 c/s), 6·52 (=CH), 2·88 and 2·97 ($CONMe_2$), 7·31 (Ph). (Found: N, 4·26. $C_{14}H_{13}F_6ON$ requires: N, 4·31%.)

Hydrogenation of cyclobutenone **28**

Cyclobutenone **28** (2·12 g) in 10 ml EtOH was hydrogenated over 0·3 g Pd black. After the absorption of H_2 ceased (7 hr), the mixture was diluted with H_2O, the oil diluted with Et_2O, dried and the solvent evaporated. The residue consisted of four substances (as determined by GLC), one of which was identical with cyclobutanone **22**; ν_{max} 1640, 1740 and 1820 cm^{-1} (CO in 4-membered ring).

3-*Phenyl-5,5,5-trifluoro-4-trifloromethylpentanoic acid* **24a**

The acid was obtained in a 65% yield by hydrogenation of **30a** over Pd black in $EtOH/H_2O$, b.p. 128°/3 mm, n_D^{20} 1·4470; ν_{max} 1505, 1610 (Ph); 1720 cm^{-1} (CO). The acid was identical (GLC and PMR) with the acid obtained from ketone **22** and H_2O. (Found: C, 48·0; H, 3·18; F, 37·6. $C_{12}H_{10}F_6O_2$ requires: C, 48·0; H, 3·33; F, 38·0%.)

Methyl-3-phenyl-5,5,5-trifluoro-4-trifluoromethylpentanoate **24b**

The ester was obtained by hydrogation of **30b** (7·3 g) in $MeOH/H_2O$ over Pd black. The yield was 3·8 g (79%), b.p. 116–117°/10 mm, n_D^{20} 1·4344; ν_{max} 1590, 1605 (Ph); 1742 cm^{-1} (CO). It was identical (GLC and PMR) with the ester, obtained from ketone **22** and MeOH; NMR F^{19}: 62·8 and 64·6 (double quartets CF_3, $J_{FF} = J_{HF} = 7·5$ c/s). (Found: C, 49·7; H, 3·82; F, 35·8. $C_{13}H_{12}F_6O_2$ requires: C, 49·7; H, 3·82; F, 36·3%.)

Anilide of 3-*phenyl-5,5,5-trifluoro-4-trifluoromethylpentanoic acid* **24c**

Acid **24a** (1·8 g) was treated with excess PCl_5 yielding the acyl chloride (1·7 g), b.p. 114–118°/16 mm, to which dissolved in 5 ml Et_2O, aniline (0·5 g) was added. After evaporating the Et_2O the residue was washed with HCl/H_2O, dried and recrystallized from heptane yielding 1·58 g (67% yield) of **24c**, m.p. 95·5°; ν_{max} 1505, 1550, 1605 (Ph); 1670 (CO); 3210, 3260–3300 cm^{-1} (NH). (Found: C, 57·7; H, 3·89; N, 3·89. $C_{18}H_{15}F_6ON$ requires: C, 57·6; H, 4·00; N, 3·74%.)

3-*Phenyl-5,5,5-trifluoro-4-trifluoromethylpentanoyl fluoride* **24d**

A mixture of **24d** and **25d** (26·9 g) with the $NEt_3 \cdot HF$ (12 g) was heated for 30 min at 100°, then poured into ice water, washed with 10%-soln of HCl/H_2O, extracted with Et_2O, dried and distilled yielding 12 g of acid **24a** and 5·1 g of acyl fluoride **24d**, b.p. 95–96°/11 mm, n_D^{20} 1·4235; ν_{max} 1500, 1610 (Ph); 1850 cm^{-1} (CO). The product was identical (PMR) with one of the components of the starting mixture. NMR F^{19}: 62·9 and 65·3 (double quartets CF_3, $J_{HF} = J_{FF} = 8·6$ c/s), −42·1 (singlet COF). (Found: C, 47·8; H, 2·95; F, 43·6 $C_{12}H_9F_7O$ requires: C, 47·7; H, 2·97; F, 44·1%.)

2,2-*Bis(trifluoromethyl)*-3,4-*dibromo*-3-*phenylcyclobutanone* (**31**)

Cyclobutenone **28** (5·4 g) and Br_2 (3·1 g) in 50 ml CCl_4 were boiled for 12 hr, then distilled yielding 7·0 g (82% yield) of **31**, b.p. 122–126°/10 mm, n_D^{20} 1·4995; ν_{max} 1490 w, 1590 w, 1625 m, 1732 m, 1800 s, 1890 sh, 1935 m; PMR: 6·25 (quartet CH, $J = 2·3$ c/s), 7·44 (Ph); NMR F^{19}: 58–59·3 (multiplet CF_3). (Found: C, 32·8; H, 1·38; Br, 35·9. $C_{12}H_6Br_2F_6O$ requires: C, 32·7; H, 1·36; Br, 36·4%.)

2,2-*Bis(trifluoromethyl)* 4-*bromo*-3-*phenyl*-3-*cyclobutenone* (**32**)

To a soln of **31** (3·5 g) in hexane (100 ml), NEt_3 (0·8 g) was added and the ppt filtered off. The filtrate was evaporated and the residue recrystallized from heptane yielding 1·4 g (50% yield) of **32**, m.p. 98·5–99°; ν_{max} 1490 m, 1550 s, 1575 m, 1592 m, 1650 w, 1692 w, 1712 w, 1730 w, 1790 vs cm^{-1} (CO); PMR: 7·7 and 8·1 (two multiplets of Ph); NMR F^{19}: 65·8 (CF_3). (Found: C, 40·7; H, 1·67; Br, 22·6. $C_{12}H_5BrF_6O$ requires: C, 40·2; H, 1·39; Br, 22·3%.)

2-*Bromo*-3-*phenyl-5,5,5-trifluoro-4-trifluoromethyl*-2-*pentenoic acid* (**34**)

Cyclobutenone **32** (0·5 g) and H_2O (0·05 g) in 40 ml acetone were kept for 24 hr at 20°, then the solvent evaporated yielding 0·52 g of the starting **32** (PMR).

Cyclobutenone **32** (0·5 g) in 5 ml of AcOH was boiled for 10 hr and then boiled for an additional hr after 1 ml H_2O had been added. After removal of the solvent under vacuum, 0·5 g crude acid **34** was obtained and reprecipitated from $NaHCO_3/H_2O$, dried and recrystallized from heptane, m.p. 124·5–125°; ν_{max} 1582 (C=C), 1690 (CO), broad 2900 cm^{-1} (OH); PMR: 5·72 (septet CH, $J = 13·3$ c/s), 7·40 (Ph), 11·9 (OH). (Found: C, 38·3; H, 1·91; F, 29·8. $C_{12}H_7BrF_6O_2$ requires: C, 38·2; H, 1·86; F, 30·3%.)

Acknowledgement—We are grateful for the contributions of N. E. Gel'man and her co-workers of the Microanalytical Laboratory, INOEC of the USSR, Academy of Sciences.

REFERENCES

[1] Yu. A. Cheburkov, I. L. Knunyants *et al.*, *Izvest. Akad. Nauk SSSR. Ser. Khim.* part: 1, 1389 (1963); part 2, 1393 (1963); part 3, 1570 (1963); part 4, 1573 (1963); part 5, 2115 (1963); part 6, 1982 (1965); part 7, 1031 (1966).

[2] J. D. Roberts and K. M. Sharts in *Organic Reactions* (Edited by A. Cope) Vol. **12**; p. 1. Wiley, New York (1962).

[3] D. C. England and C. G. Krespan, *J. Am. Chem. Soc.* **88**, 5582 (1966).

[4] Yu. A. Cheburkov, N. Mukhamadaliev and I. L. Knunyants, *Isvest. Akad. Nauk SSSR, Ser. Khim.* 383, 384, 1868 (1966).

[5] R. Huisgen, L. Feiler and G. Binsh, *Angew. Chem. Int.* **3**, 753 (1964); R. H. Hasek and J. C. Martin, *J. Org. Chem.* **26**, 4775 (1961); **28**, 1468 (1963); J. C. Martin and R. H. Meen, *Ibid.* **30**, 4311 (1965); R. H. Hasek, P. G. Gott and J. C. Martin, *Ibid.* **31**, 1931 (1966); G. Opitz, H. Adolph, M. Kleemann and F. Zimmermann, *Angew. Chem.* **73**, 654 (1961); G. Opitz, M. Kleemann and F. Zimmermann, *Ibid.* **74**, 32 (1962); G. Opitz and F. Zimmermann, *Liebigs Ann.* **662**, 178 (1963); G. Opitz and M. Kleemann, *Ibid.* **665**, 114 (1964); G. A. Berchtold, G. R. Harvey and G. E. Wilson, Jr., *J. Org. Chem.* **26**, 4776 (1961); **30**, 2642 (1965).

[6] D. C. England and C. G. Krespan, *J. Am. Chem. Soc.* **87**, 4019 (1965).

[7] A. P. Krapcho and G. H. Lesser, *J. Org. Chem.* **31**, 2030 (1966).

[8] H. Staudinger and E. Suter, *Ber. Dtsch. Chem. Ges.* **53**, 1092 (1920).

[9] E. H. Farmer and M. O. Farooq, *J. Chem. Soc.* 1925 (1938); K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kuhlhorn and J. Schneider, *Liebigs Ann.* **589**, 122 (1954); T. J. Katz and R. Dessau, *J. Am. Chem. Soc.* **85**, 2172 (1963).

[10] E. H. Farmer and M. O. Farooq, *Chem. & Ind.* 1079 (1937).

[11] J. C. Martin, P. G. Gott, V. W. Goodlett and R. H. Hasek, *J. Org. Chem.* **30**, 4175 (1965).

[12] H. Bestian and D. Günter, *Angew. Chem. Int.* **2**, 608 (1963).

[13] G. Spengler, *Angew. Chem.* **61**, 308 (1949); J. R. Van der Bij and E. C. Kooyman, *Rec. Trav. Chim.* **71**, 837 (1952).

[14] S. Searler, Jr., *Heterocyclic Compounds with Three and Four membered Rings* (Edited by A. Weissberger), Part II, Vol. **19**; p. 984. Interscience Division of Wiley, New York, London, Sydney (1964).

[15] G. Quadbeck, *Angew. Chem.* **68**, 361 (1956).

[16] R. N. Lacey in *Advances in Organic Chemistry, Methodes and Results* (Edited by R. A. Raphael) Vol. II; p. 213. Interscience Division of Wiley, New York (1960).

[17] J. C. D. Brand and G. Eglinton, *Application of Spectroscopy to Organic Chemistry* p. 64, Oldbourne Press, London (1965).

[18] M. O. Farooq, T. A. Vahidy and S. M. Hussain, *Bull. Soc. Chim. Fr.* 830 (1958).

[19] E. Vogel and K. Müller, *Liebigs Ann.* **615**, 29 (1958).

[20] V. N. Dashkevich, *Nauch. Zapiski Uzhgorod. Univ.* **18**, 11 (1957); *Chem. Abstr.* **54**, 12015c (1960).

[21] R. N. Lacey, *The Chemistry of Alkenes* (Edited by S. Patai) p. 1161. Interscience Division of Wiley, New York, London, Sydney (1964); J. Etienne and N. Fisher, *The Chemistry of Heterocyclic Compounds with Three and Four membered Rings* (Edited by A. Weissberger) part II; Vol **19**; p. 729. Interscience Division of Wiley, New York, London, Sydney (1964); H. E. Zaugg, *Organic Reactions* (Edited by R. Adams) Vol. **8**; p. 305. Wiley, New York (1954).

[22] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.* **83**, 1226 (1961).

[23] C. S. Marvel and M. I. Kohan, *J. Org. Chem.* **16**, 741 (1951).

[24] H. Staudinger and A. Rheiner, *Helv. Chim. Acta* **7**, 8 (1924).

[25] E. Bergmann and O. Blum-Bergmann, *J. Chem. Soc.* **1938**, 727.

[26] I. L. Knunyants, S. T. Kocharyan, Yu. A. Cheburkov, M. D. Bargamova and E. M. Rokhlin, *Dokl. Akad. Nauk SSSR* **165**, 827 (1965).

[27] H. E. Simmons, Jr., B. S. Thesis, Massachusetts Institute of Technology; *J. Am. Chem. Soc.* **86**, 2645 (1964); Ref. 32.

[28] H. Staudinger, *Liebigs Ann.* **356**, 51 (1907).

[29] C. L. Agre. Ph.D. Thesis, University of Minnesota, p. 77 (1937); *J. Am. Chem. Soc.* **61**, 2619 (1939), Ref. 31.

[30] L. I. Smith and H. H. Hoehn, *Ibid.* **61**, 2619 (1939) **63**, 1175, 1181 (1941).

[31] J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *J. Am. Chem. Soc.* **75**, 4765 (1953); E. J. Smutny and J. D. Roberts, *Ibid.* **77**, 3420 (1955); E. F. Silversmith and J. D. Roberts, *Ibid.* **80**, 4083 (1958); E. J. Smutny, M. C. Caserio and J. D. Roberts, *Ibid.* **82**, 1793 (1960). Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *Ibid.* **82**, 3106 (1960). K. Nagarajan, M. C. Caserio and J. D. Roberts, *Ibid.* **86**, 449 (1964). S. L. Manatt, M. Vogel, D. Knutson and J. D. Roberts, *Ibid.* **86**, 2645 (1964).

[32] E. F. Jenny and J. D. Roberts, *Ibid.* **78**, 2005 (1956).

[33] E. F. Silversmith, Y. Kitahara, M. C. Caserio and J. D. Roberts, *Ibid.* **80**, 5840 (1958).

[34] E. F. Jenny and J. Druey, *Ibid.* **82**, 3111 (1960).

[35] E. F. Silversmith, Y. Kitahara and J. D. Roberts, *Ibid.* **80**, 4088 (1958).

[36] Stuart-Briegleb Model, Eugon Atom model, 1949–1959.

[37] M. Takahashi, D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.* **84**, 2935 (1962).

[38] F. A. L. Anet, A. J. R. Bourn, P. Carter and S. Winstein, *Ibid.* 87, 5249 (1965).

[39] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.* **35**, 1243 (1961).

[40] T. A. Wittstruck, S. K. Malhotra, H. Ringold and A. D. Cross, *J. Am. Chem. Soc.* **85**, 3038 (1963); P. C. Myhre, J. W. Edmonds and J. D. Kruger, *Ibid.* **88**, 2459 (1966); S. T. Yoffe, E. I. Fedin, P. V. Petrovskii and M. I. Kabachnik, *Tetrahedron Letters* No. 24, 2661 (1966); Yu. A. Cheburkov, Yu. E. Aronov, E. I. Fedin, P. V. Petrovskii and I. L. Knunyants, *Dokl. Akad. Nauk SSSR* **169**, 128 (1966) and Refs cited there.

[41] J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.* **87**, 3884 (1965).

[42] Yu. A. Cheburkov, N. Mukhamadaliev, N. S. Mirsabekyants and I. L. Knunyants, *Izvest. Akad. Nauk SSSR, Ser. Khim.* 1265 (1966).