bis(TRIFLUOROMETHYL)KETENE

IX.* DIMERIZATION UNDER THE ACTION OF WEAK BASES AND REACTION WITH TRIETHYL PHOSPHITE†

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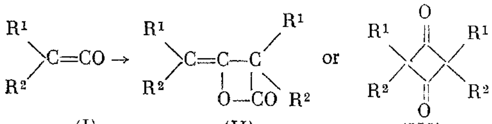
Ketene dimers were obtained simultaneously with ketenes [3], and up until recently it was thought that monoalkylketenes (I, $R^1 = H$) formed β-lactone dimers (II), while disubstituted ketenes formed cyclobutanedione dimers (III) [4, 5].

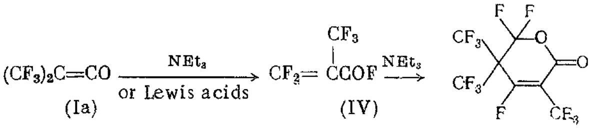


(I) (II) (III)

or $R^1 = R^2 = CF_3$.

Although the greater part of available data falls into this scheme, at present monoalkylketene dimers are known which have the cyclobutanedione structure [6, 7], and β-lactone dimers of dimethyl- and diphenylketene have been prepared [8-10]. Systematization of literature information [7] leads to the conclusion that any pure ketene spontaneously dimerizes to the cyclobutanedione dimer (III) (see, however, reference [11]). The β-lactone dimers (II) are obtained as the result of a catalyzed process in which tertiary amines or their hydrochlorides [7, 12], sodium methoxide [8], N-methylimidazole [9], Lewis acids [7, 13] or triethyl phosphite [10] are all effective as catalysts. (For more detailed discussion of ketene dimerization, see reference [14].)

bis(Trifluoromethyl)ketene (Ia) does not dimerize spontaneously [15], but under the action of Lewis acids undergoes isomerization [16] into perfluoromethacrylyl fluoride (IV). Triethylamine also causes this isomerization, but the end-product is a dimer of the acid fluoride (IV) – the δ-lactone (V) [15, 17].



(Ia) (IV) (V)

We have shown that bases with reduced electron density on nitrogen compared to triethylamine, such as diethylnitrosoamine, tetraalkylureas, or dimethylacetamide, or also triethyl phosphate, are not capable of causing the isomerization of bis(trifluoromethyl)ketene to acid fluoride (IV). Under the catalytic action of these substances bis(trifluoromethyl)ketene forms the β-lactone dimer (IIa). Dimer (IIa) is a colorless, mobile liquid with an agreeable odor; inhalation of a small amount of its vapor causes a severe headache. The dimerization catalysts listed above do not dissolve in lactone (IIa) in the cold, and as the dimerization of ketene (Ia) proceeds, they separate in the form of an upper layer. Heating increases the mutual solubility of lactone (IIa) and the base, the mixture becomes homogeneous, and a vigorous decomposition of dimer (IIa) takes place in it, accompanied by cleavage of a hydrogen atom from the catalyst.

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[*] Previous communications, see references [1, 2].

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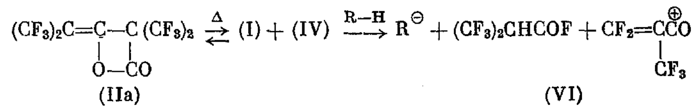
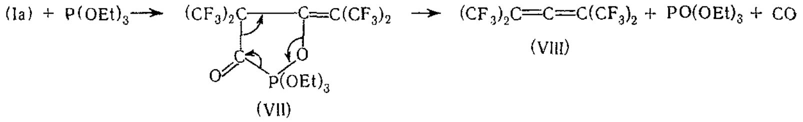


$$\underset{\text{(IIa)}}{\underset{O-CO}{(CF_3)_2C{=}C{-}C(CF_3)_2}} \underset{\leftarrow}{\overset{\Delta}{\rightarrow}} (I) + (IV) \xrightarrow{R-H} R^{\ominus} + \underset{\text{(VI)}}{(CF_3)_2CHCOF} + \underset{CF_3}{CF_2{=}C\overset{\oplus}{C}O}$$

Hexafluoroisobutyryl fluoride (VI) is formed as a result of this reaction. Diethylnitrosoamine and dimethylacetamide cause the decomposition of dimer (IIa) particularly easily on mild warming. Dimethylnitrosoamine, in distinction from diethylnitrosoamine, has appreciable solubility in lactone (IIa) and therefore an attempt to use it as a dimerization catalyst for bis(trifluoromethyl)ketene led to the formation of acid fluoride (VI) as the sole reaction product. The most successful dimerizing agent proved to be tetramethylurea, use of which gives lactone (IIa) in close to quantitative yields.

There is a remarkable difference in the reaction of bis(trifluoromethyl)ketene with such pairs of related substances as ethyl nitrite-diethynitrosoamine or dimethylformamide-dimethylacetamide, which do differ, however, in their basicity. The first compounds in the indicated pairs – ethyl nitrite [18] and dimethylformamide [19] – add to ketene (Ia), while the latter ones, which are stronger bases, dimerize it.

A still greater difference is observed in the actions of compounds of trivalent and pentavalent phosphorus on ketene (Ia). As has been said above, triethyl phosphate dimerizes ketene (Ia), but triethyl phosphite enters into a new interesting reaction with it, as a result of which tetrakis(trifluoromethyl)allene (VIII), triethyl phosphate and carbon monoxide are formed.



The one of the possible reaction schemes which is presented here includes the intermediate formation of a five-membered phosphorus-containing cyclic compound (VII) from two molecules of ketene (Ia) and one molecule of triethyl phosphite and its subsequent decomposition into the reaction products. In favor of this hypothesis is the fact that mixing the reagents at a temperature below 0° gives a homogeneous product which crystallizes on more intense cooling [probably compound (VII)]; further, on warming to 0°, carbon monoxide is evolved and the allene (VIII) gradually separates in the form of a colorless lower layer. It is difficult to say much of the special features of bis(trifluoromethyl)ketene in the reaction with triethyl phosphite, since this reaction has hardly been studied with ordinary ketenes. It is only known that diphenylketene is

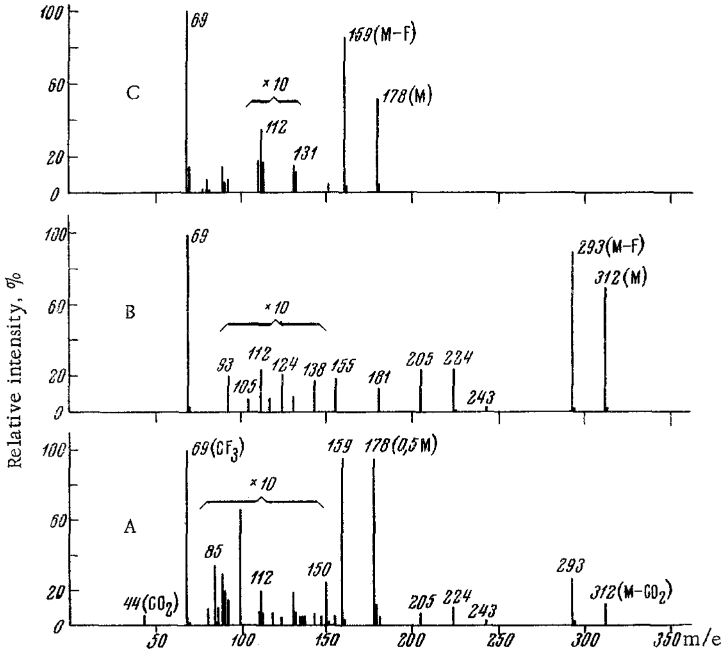
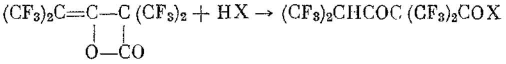


Fig. 1. Mass spectra: A) dimer (IIa); B) allene (VIII); C) ketene (Ia).

converted into tolane under the action of triethyl phosphite [20], while dimethylketene (I, R = CH_3) forms a β-lactone dimer (II) [10]. It is possible that in the example we have studied the first reaction stage is formation of a β-lactone dimer (IIa). In any case, a specially conducted experiment showed that this dimer reacts with triethyl phosphite to form these same products – allene (VIII), triethyl phosphate and CO: (IIa) + $P(OEt)_3 \rightarrow$ (VIII) + $PO(OEt)_3$ + CO.

The β-lactone structure dimer (IIa) and the structure of allene (VIII) follow from their NMR and infrared spectra, which are given in the experimental section. Besides this, mass-spectra were studied.* The mass-spectrum of dimer (IIa) (Fig. 1A) is, as it were, a superposition of the spectra of three substances: allene (VIII) (Fig. 1B), the ketene (Ia) (Fig. 1C) and CO_2. It was not possible to detect the molecular ion of dimer (IIa).

The chemical reactions of dimer (IIa) and allene (VIII) which are discussed below also confirm the proposed structures of these compounds. The β-lactone dimer (IIa), in agreement with expectations and like the unfluorinated analog [10], is smoothly decarboxylated in the vapor phase on contact with a nichrome spiral heated to 800°, forming allene (VIII): (IIa) → (VIII) + CO_2 (see reference [15]). Dimer (IIa) has a clearly defined electrophilic character. It reacts readily with alcohols, thiols, amines or ammonia at low temperatures in the absence of a catalyst, giving numerous derivatives (IX) of tetrakis(trifluoromethyl)-acetoacetic acid (IXa).



$$\underset{(IIa)}{\underset{\displaystyle O-CO}{(CF_3)_2C=C-C(CF_3)_2}} + HX \rightarrow \underset{(IX)}{(CF_3)_2CHCOC(CF_3)_2COX}$$

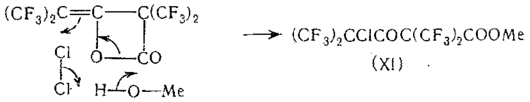
	a	b	c	d	e	f	g	h
X=	OH,	MeO,	EtO,	PhO,	EtS,	PhS,	NH_2,	PhNH

The reaction with water probably leads to formation of the acid itself (IXa), which, however, cannot be isolated because of its easy decarboxylation to tetrakis(trifluoromethyl)acetone (X).

$$(IXa) \rightarrow \underset{(X)}{(CF_3)_2CHCOCH(CF_3)_2} + CO_2$$

The products of the given ring cleavage reactions of lactone (IIa) do not differ from those obtained in reactions of β-lactone dimers of other ketenes [5]. Below we show two reactions of dimer (IIa) which have no counterpart in the unfluorinated compound series.

Dimer (IIa) is not chlorinated on prolonged irradiation with ultraviolet light. In a sealed ampule containing a homogeneous solution of dimer (IIa) and chlorine in CCl_4, chlorination still does not take place on prolonged heating; on cooling, the starting dimer (IIa) is isolated from the solution quantitatively in the form of a colorless lower layer. However, when methanol is added to the homogeneous solution mentioned above, dimer (IIa) enters into an interesting reaction of conjugated addition, which leads to an ester of γ-chlorotetrakis(trifluoromethyl)acetoacetic acid (XI).



Apparently, because of its increased electrophilicity, β-lactone dimer (IIa) is incapable of reacting with chlorine, but on addition of methanol reaction is started by a nucleophilic attack of the methoxy group on the carbonyl group of the lactone, with subsequent addition of a chlorine cation. Thus, here there is a rare case where conjugate addition is initiated by an attack of an anionoid particle (see reference [21] for similar reactions).

Another uncommon reaction of the β-lactone dimer (IIa) is its reaction with dimethylformamide, which leads to formation of bis(trifluoromethyl)ketone, hexafluoroisobutenyldimethylamine (XII) and CO_2 {we did not isolate the known [19] enamine, but it was at once hydrolyzed to hexafluoroisobutyraldehyde (XIII)}.

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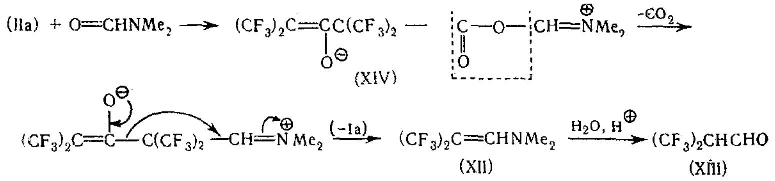
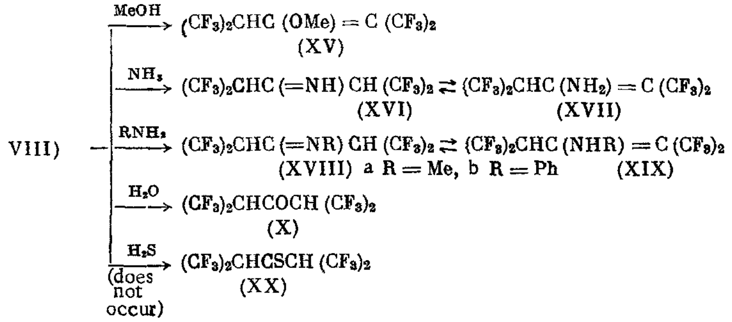
*Mass-spectra were taken by R. G. Kostyanovskii, V. P. Nichiporenko, and R. S. Lachinov in an MKh-1303 instrument, V = 30 volts, I = 0.75 amperes.



In this reaction, dimethylformamide, just as in the reactions we have previously described with bis(trifluoromethyl)ketene [19] or with acid chlorides of easily decarboxylated acids [22], probably attacks the electrophilic carbon atom of the β-lactone dimer (IIa) carbonyl group with its nucleophilic center, which is located on the oxygen atom. The bipolar ion (XIV) which is formed thereby loses CO_2 and decomposes into the ketene (Ia) and the enamine (XII). Under the reaction conditions, part of the ketene (Ia) is removed along with the carbon dioxide evolved and does not have time to react with excess dimethylformamide. Thus, dimethylformamide practically causes monomerization of the β-lactone dimer (IIa).

We have also studied in detail the properties of tetrakis(trifluoromethyl)allene which has been prepared for the first time, and which, in contrast to the simplest perfluoroallene [23], turned out be a very stable compound. Thus, it is not polymerized on storage; it is not changed on passage over KF or glass wool up to 500°. At a higher temperature (up to 800° over KF or in a quartz capillary) allene (VIII) also remains unchanged, but part of it is carbonized under these conditions. Allene (VIII) does not participate in a Diels–Alder reaction with butadiene at 100°; it is not chlorinated on irradiation, does not add FNO, and does not react with atomic hydrogen.*

However, allene (VIII) reacts readily with water, alcohols, ammonia or amines, whereupon the attack of the nucleophilic part is directed toward the central atom; the addition products (X), (XV), (XVI), and (XVIII) are formed thereby, respectively.



The electrophilicity of the derivatives (XV), (XVI), and (XVIII) so obtained is insignificant, thus, ether (XV) does not add a second methanol molecule, and the methylamine (XVIIIa) is incapable of adding a second molecule of methylamine. It is very possible that the compounds obtained by addition of ammonia and amines to allene (VIII) are equilibrium mixtures of the imines (XVI), (XVIII) and enamines (XVII), (XIX). The splitting of the imine absorption band in the infrared spectrum of compound (XVI) and the presence in this same compound of two NH- group absorption frequencies speaks in favor of this assumption. A comparison of the intensity of signals from the protons of the CH- and NH- groups of imine (XVI) and the CH- and C_6H_5- groups of anil (XIXb) in their PMR spectra also serves as evidence in favor of tautomerism. The presence of enamine (XVII) in the equilibrium mixture follows from the F^{19} NMR spectrum: two quartets of the $(CF_3)_2C=$ group. However, additional investigation is required for final establishment of tautomerism.

Being a very active electrophile, allene (VIII) nevertheless does not add ethyl mercaptan or thiophenol on extended heating. It was not possible either to obtain tetrakis(trifluoromethyl)thioacetone (XX) by addition of hydrogen sulfide to allene (VIII). No reaction was observed on heating allene (VIII) with excess liquid hydrogen sulfide in dioxane or without the solvent, nor in the presence of sodium hydrosulfide. When sulfolane was used as solvent, allene (VIII) reacted easily with a mixture of H_2S and NaSH, but thioketone (XX) was not formed thereby, but rather a product of hydrogenation of one double bond of the allene-olefin (XXI), and sulfur was liberated.

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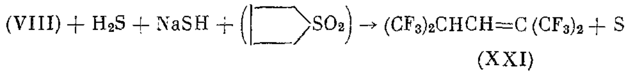
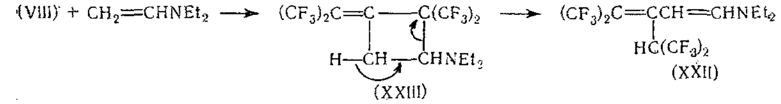
* The reaction with hydrogen was studied by V. V. Bukhtiyarov (now deceased). Monitoring was carried out by the nature of the EPR signal.



It is possible that the first act in this reaction is cleavage of a hydride ion from NaSH by allene (VIII), with subsequent addition of a proton from hydrogen sulfide. Sulfolane facilitates the reaction, playing the usual role of a solvent which solvates cations.

An unexpected reaction takes place when allene (VIII) is brought together with triethylamine. The reaction products are the olefin (XXI) and the dienamine (XXII).

$$\underset{\text{(VIII)}}{(CF_3)_2C{=}C{=}C(CF_3)_2} \xrightarrow{NEt_3} \underset{\text{(XXI)}}{(CF_3)_2CHCH{=}C(CF_3)_2} + CH_2{=}CHNEt_2$$



In the first stage of this unusual reaction, the allene (VIII) dehydrogenates triethylamine. Thereupon olefin (XXI) is formed, plus probably diethylvinylamine. A possible route for the conversion of the latter to dienamine (XXII) is cyclodimerization with a second molecule of allene (VIII) to form the aminocyclobutane (XXIII), which is isomerized with ring cleavage into the final reaction product, (XXII).

This result – hydrogenation of allene (VIII) by triethylamine – can be described in terms of reactions taking place in complexes with charge transfer (see reference [24] about such reaction); the formation of a complex of the electrophilic allene (VIII) with the nucleophilic triethylamine is rather probable.

EXPERIMENTAL

Boiling points and melting points are not corrected. Chromatographic analysis (GLC) of reaction mixtures and purity checking of compounds was carried out in the following columns: A) this consisted of two parts: 20% "Rheoplex" on "Chromosorb B" and 20% polyethylene glycol 400 on "Chromosorb P," treated with hexamethyldisilazane; B) 20% fuel oil on fire brick; C) type 1 thiokol of the synthetic rubber factory on firebrick; D) 1,4-butanediol devalerate on "Chromosorb P"; E) liquid polytrifluorochloroethylene on "Fluoroplast 3." The gas chromatographic analysis was carried out at temperatures close to the boiling point. Analysis of the compounds (IIa), (VIII), (Ia), and (VI) was additionally carried out by chromatographing the esters (IXb), (XV), and $(CF_3)_2CHCOOMe$ (XXIV), respectively, formed on treatment of the indicated compounds or their mixtures with methanol. Infrared spectra were taken in a UR-10 spectrophotometer. NMR spectra were recorded on a "Hitachi" H-6013 spectrometer. In all cases where this is not stipulated separately, 50% solutions of samples in CCl_4 were used; and HMDS (0.05 δ from TMS) or Freon 112 (69 τ or $CFCl_3$) were used as internal standards. Chemical shifts are given on the δ-scale relative to TMS or the τ-scale relative to $CFCl_3$.

β-Lactone Dimer of bis(Trifluoromethyl)ketene(IIa). 1) A mixture of 42 g of (Ia) and 7 g of $(Et_2N)_2CO$ was allowed to stand 24 h at 20° (the initially homogeneous solution separated into layers after 2 h). The lower layer was separated after cooling and was fractionated in a column under vacuum. There was obtained 39.2 g (93%) of (IIa), bp 48° (149 mm); 92° (745 mm); n_D^{20} 1.3091. Found %: C 26.9; F 64.6. $C_8F_{12}O_2$. Calculated %: C 27.0; F 64.0. IR spectrum (ν_{max}, cm^{-1}): 1730 (C=C) v.s; 1890 m; 1935 s, 1970 m; 2010 w. F^{19} NMR spectrum: 62.4 ($CF_3C{=}$ quartet, $J_{(F-F)}$ 8.04 Hz); 64.1 ($CF_3C{=}$ multiplet, $J_{(F-F)}$ 8.04 Hz); 68.3 [$(CF_3)_2C$ quartet, $J_{(F-F)}$ 6.42 Hz].

2) The reaction was carried out similarly to the preceding example, but 0.1 mole of $(Et_2N)_2CO$ was used per mole of ketene (Ia). The yield of (IIa) was 90-95%.

3) Equimolar amounts of (Ia) and Et_2NNO were allowed to stand at 0° for one day, the lower layer of dimer (IIa) was carefully separated, taking care that no drop of Et_2NNO got into it, and it was distilled under vacuum into a trap; and then it was fractionated in a column. Yield of (IIa), about 65%.

4) Equimolar amounts of (Ia) and $PO(OEt)_3$ were allowed to stand one day at 20°. A mixture of 60% (Ia) and 40% (IIa) was obtained [gas chromatography of the corresponding esters (XXIV) and (IXb)].

5) Equimolar amounts of (Ia) and dimethylacetamide were allowed to stand for a day at 0°. A mixture (by g.c.) of 10% (Ia), 58% (VI), 20% (IIa) and 12% (VIII) was obtained.

6) Equimolar amounts of (Ia) and Me_2NNO were allowed to stand 4 h at 0°. The homogeneous mixture was distilled. There was obtained 42% of (VI), bp 35°, identical (by g.c., columns C and E) to a known sample [25].

Decomposition of Dimer (IIa). 1) Dimer (IIa) was heated with an equimolar amount of Et_2NNO at 70°. Thereupon the acid fluoride (VI) distilled out, yield 50%°

2) Dimer (IIa) (4 g) was heated with 1.3 g of Me_2NCOMe for 4 h at 60°. A mixture (2.1 g, 50%) of products was distilled into a trap at −78°; it had bp 34-35° on subsequent distillation and consisted (g.c.) of 7% allene (VIII) and 93% acid fluoride (VI). A similar ratio was obtained on chromatographing the mixture of esters [(XV) and (XXIV)] obtained on treatment of the product with methanol.

Tetrakis(trifluoromethyl)allene (VIII). To 80.7 g of (Ia) was added at 0°, with stirring, 32 g of $P(OEt)_3$ which had been stored over Na. Thirty minutes after addition of the phosphite, evolution of CO began (identified by test with $PdCl_2$, burned, and did not contain CO_2), which continued for about 3 h at 0° and still another hour at 20°. On the next day the colorless lower layer was separated and distilled. A yield of 53.7 g (76%) of (VIII), bp 41° (743 mm), was obtained, n_D^{20} 1.275. Found %: C 26.8; F 73.1. C_6F_{12}. Calculated %: C 26.8; F 73.0. IR spectrum (ν_{max}, cm^{-1}): 1530-1660 (broad) w, 1760-1850 (broad) w; 2025 (C=C =C) s. F^{19} NMR spectrum, 65.6 (CF_3 singlet). The upper layer, bp 63-64° (3 mm), consisted of 85% $PO(OEt)_3$ and a mixture of unidentified products (g.c., columns A and B).

2) Dimer (IIa) (2.88 g) was pyrolyzed in a ketene lamp type of apparatus on a nichrome spiral heated to 800°. Carbon dioxide was evolved and swept 2.02 g (80%) of (VIII) into a trap at −78°.

3) To dimer (IIa) (1.7 g) at −78° was added 0.8 g of $P(OEt)_3$. On warming to 0° a vigorous reaction took place and 110 ml of CO was evolved ($PdCl_2$ test, burns, passes quantitatively through 50% KOH). Compound (VIII), (1.2 g, 65%) was distilled from the remaining mixture into a trap cooled to −78°. The residue contained 80% $PO(OEt)_3$ in a mixture with unidentified materials (g.c. analysis).

Reactions of β-Lactone Dimer (IIa). With Methanol. To 3.4 g of dimer (IIa) at −78° was added an excess of methanol, and the mixture was slowly warmed to 20°. After 1 h, it was washed with water, dried and distilled. There was obtained 3.5 g (94%) of (IXb), bp 76-78° (34 mm), n_D^{20} 1.3243. Found %: C 27.2; H 1.08; F 58.3. $C_9F_{12}H_4O_3$. Calculated %: C 27.8; H 1.03; F 58.9. IR spectrum (ν_{max}, cm^{-1}): 1755 v.s, 1783 (C=O) v.s. PMR spectrum: 3.92 (CH_3); 4.98 (CH heptet, J 7.5 Hz). F^{19} NMR spectrum: 66.3 (CF_3 multiplet).

With Ethanol. Similarly to the preceding experiment, from 1.2 g of (IIa) there was obtained 1.1 g (81%) of (IXc), bp 160-161° (737 mm), n_D^{20} 1.3270. Found %: C 29.8; H 1.49. $C_{10}F_{12}H_6O_3$. Calculated %: C 29.8; H 1.49. IR spectrum (ν_{max}, cm^{-1}) 1758 plateau; 1780 (C=O) v.s. PMR spectrum: 1.38 (CH_3 triplet); 4.45 (CH_2 quartet); 4.61 (CH heptet, J 6.85 Hz).

With Phenol. To 1.9 g of dimer (IIa) in 3.5 ml of absolute ether was added 1 g of phenol and ether was added until the mixture was homogeneous. After 2 days the ether was distilled off, the residue was washed with aqueous $NaHCO_3$, dried and distilled. There was obtained 1 g (42%) of (IXd), bp 97° (12 mm); n_D^{20} 1.3829. Found %: C 37.3; H 1.33; F 50.7. $C_{14}F_{12}H_6O_3$. Calculated %: C 37.4; H 1.33; F 50.8. IR spectrum (ν_{max}, cm^{-1}): 1755 s, 1790 s (C=O). PMR spectrum: 4.90 (CHheptet, J 6.0 Hz); 6.85-7.50 (C_6H_5).

With Ethyl Mercaptan. At 20°, 1.5 g of (IIa) was mixed with an equal volume of EtSH, ether was added until the mixture was entirely homogeneous, and the mixture was allowed to stand overnight. After stripping excess mercaptan and ether, 1.2 g (68%) of (IXe) was obtained, bp 113-115° (86 mm); n_D^{20} 1.3662. Found %: C 28.7; H 1.65; F 54.4. $C_{10}F_{12}H_6O_2S$. Calculated %: C 28.7; H 1.44; F 54.4. IR spectrum (ν_{max}, cm^{-1}): 1670 s, 1700 m, 1750 s (C=O). PMR spectrum: 1.31 (CH_3 triplet); 3.05 (CH_2 quartet); 4.79 (CH heptet, J 6.55 Hz).

With Thiophenol. Thiophenol (1.6 g) and 3.44 g of (IIa) were mixed, and after 2 h the mixture was distilled. There was obtained 3.31 g (74%) of (IXf), bp 111° (7 mm); n_D^{20} 1.4224. Found %: C 36.0; H 1.37; F 49.1. $C_{13}F_{12}H_6O_2S$. Calculated %: C 36.0; H 1.29; F 49.0. IR spectrum (ν_{max}, cm^{-1}): 1695 v.s, 1710 plateau; 1760 v.s (C=O). PMR spectrum: 4.86 (CH heptet, J 6.8 Hz); 7.35 (C_6H_5).

With Ammonia. To 0.1 ml of liquid anhydrous ammonia at −78° was added 5 ml of absolute ether and 1 g of (IIa). After an hour the mixture was warmed to 20° and the solvent was evaporated. There was obtained 0.98 g (91%) of (IXg), mp 161-162° (after two recrystallizations from EtOH−heptane and toluene). Found %: C 25.7; H 0.77; N 3.94. $C_8F_{12}H_3NO_2$. Calculated %: C 25.7; H 0.80; N 3.75. IR spectrum (ν_{max}, cm^{-1}): 1500 m, 1770 s. PMR spectrum: 5.31 (CH heptet, J 6.85 Hz), in acetone.

With Aniline. A mixture of 4.25 g of (IIa) in 15 ml of ether and 1.1 g of aniline was allowed to stand overnight at 0°. After evaporation, a yellow oil was obtained which was a mixture of three substances (thin-layer chromatography on silica gel containing 10% H_2O, development with a mixture of acetone and hexane, 1: 2). Compound (IXh) was purified chromatographically (silica gel containing 10% H_2O; eluent, benzene); the fraction was monitored by the fluorescence of a drop of eluate on filter paper under ultraviolet light). There was obtained 3.3 g (62%) of (IXh), mp 36-37° (from hexane). Found %: C 37.2; H 1.53; F 51.4; N 3.25. $C_{14}F_{12}H_7NO_2$. Calculated %: C 37.5; H 1.56; F 50.1; N 3.12. IR spectrum (ν_{max}, cm^{-1}): 1500 s, 1600 m, 1730 v.s, 1750 v.s. PMR spectrum: 4.93 (CH heptet, J 7.29 Hz); 7.08-7.58 (C_6H_5).

With Water. To 3.1 g of dimer (IIa) was added an equal volume of water and the mixture was allowed to stand two days until CO_2 evolution ceased. The crystals were pressed out on filter paper (they could not be filtered because of the very appreciable volatility of the product), 1 ml of conc. H_2SO_4 was added, and the mixture was distilled. There was obtained 2.6 g (93%) of (X), with a strong specific aroma, bp 102°, mp 71.5-72° (in sealed capillary). Found %: C 25.5; H 0.62; F 68.7. $C_7F_{12}H_2O$. Calculated %: C 25.5; H 0.62; F 69.1. IR spectrum (ν_{max}, cm^{-1}): 1740 m, 1764 v.s (C=O). PMR spectrum: 4.81 (CH heptet, J 6.1 Hz) in tetrahydrofuran. F^{19} NMR spectrum: 66.7 (CF_3 doublet, J 6.43 Hz).

With Dimethylformamide. To 7.83 g of (IIa) was added 5 ml of dimethylformamide. A reaction slowly took place on the surface of the layer interface, with gas evolution. On heating to 45°, the mixture became homogeneous after an hour; 220 ml of a mixture of CO_2 and CO was evolved thereupon. In an attached trap, cooled to −78°, 3 g of a liquid was condensed, which boiled over the range 5-45° and consisted of 72% ketene (Ia) (28% yield) and 28% allene (VIII) (12% yield (composition from g.c. analysis). The residue was treated at 0° with 10 ml of conc. HCl and 4 g (51%) of (XIII) was distilled off, bp 49°, identical with a known sample [19] by g.c. on column B and by PMR spectroscopy.

Methyl γ-Chlorotetrakis(trifluoromethyl)acetoacetate. A mixture of 10 g of (IIa) in 30 ml of CCl_4 and 2 ml of liquid chlorine was irradiated with ultraviolet light for 5 h. The contents of the ampule was divided into two equal parts. To one half was added an excess of methanol, and after 1 h the mixture was distilled. There was obtained 4.53 g (76%) of (XI), bp 53° (7 mm); n_D^{20} 1.3621. Found %: C 25.2; H 0.60; Cl 8.40. $C_9F_{12}ClH_3O_3$. Calculated %: C 25.6; H 0.71; Cl 8.54. IR spectrum (ν_{max}, cm^{-1}): 1748 s, 1770 m, 1790 s (C=O). PMR spectrum: 4.00 (CH_3). F^{19} NMR spectrum: 65.4 and 71.05 (CF_3 multiplets). The second half was cooled to −10°; the colorless lower layer was separated and distilled. There was obtained 4.9 g of (IIa), bp 92°; after treatment with methanol it gave ester (IXb).

Reactions of Tetrakis(trifluoromethyl)allene (VIII). Compound (VIII) (2.1 g) was passed twice, in a stream of dry argon, through a glass tube heated to 500° for a 50 cm length, which was filled with a) glass wool; b) ignited KF. In a trap cooled to −78° was condensed 2.1 g of starting compound (VIII) (by g.c. analysis), which was converted into (XV) by treatment with methanol.

Compound (VIII) (3.2 g) was passed, in a stream of dry argon: a) through a quartz capillary; b) through a quartz tube filled with ignited KF, heated to 800° along a 50 cm length. Starting compound (VIII) (1.92 g, 60%) was condensed in a trap −78°.

With Methanol. Compound (VIII) (1.14 g) was mixed, with cooling, with an equal volume of methanol, and the mixture was carefully heated to 30°; 1 h after complete homogeneity had been attained the mixture was washed with water, dried and distilled. Compound (XV) (1.06 g, 85%) was obtained, bp 103-105° (738 mm); n_D^{20} 1.3100. Found %: C 27.8; H 0.69; F 67.1. $C_8F_{12}H_4O$. Calculated %: C 27.9; H 1.16; F 66.4. IR spectrum (ν_{max}, cm^{-1}): 1648 (C=C), s. PMR spectrum, 4.21 (CH_3); 4.42 (CH heptet, J 7.42 Hz). F^{19} NMR spectrum: 57.7 and 60.9 (CF_3C= group quartets, $J_{(F-F)}$ 9.66 Hz), 65.8 [$(CF_3)_2CH$ doublet, $J_{(H-F)}$ 8.10 Hz, with weak splitting of components].

With Ammonia. A mixture of 0.4 g of anhydrous liquid ammonia in 25 ml of absolute ether and 7.35 g of (VIII) was allowed to stand 3 h at −78° and 12 h at 0°. After stripping off the ether in a column there was obtained 3.2 g (42%) of (XVI), bp 67° (117 mm); n_D^{20} 1.3233. Found %: C 25.6; H 1.04; F 69.3; N 4.36. $C_7F_{12} \cdot H_3N$. Calculated %: C 25.6; H 0.92; F 69.3; N 4.26. IR spectrum (ν_{max}, cm^{-1}): 1625 (C=N) s, 1665 (C=C) s, 3060 (CH) s, 3470 and 3560 (NH) v.s. PMR spectrum: 4.54 (CH heptet, J 7.3 Hz; 1.5 H); 5.20 (broad NH; 1.5 H). F^{19} NMR spectrum: 52.75 and 59.0 (broadened quartet and quartet of CF_3C= groups, $J_{(F-F)}$ 9.69 Hz), 66.7 [doublet $J_{(H-F)}$ 8.04 Hz of quartets $J_{(F-F)}$ 1.6 Hz of $(CF_3)_2CH$ group].

With Methylamine. A mixture of 11.72 g of (VIII) in 15 ml of Freon 113 and 1.67 g of methylamine in 10 ml of absolute ether was allowed to stand 3 h at −78° and 12 h at 0°. After the solvents had been stripped off, 6.78 g (53%) of (XVIIa) was obtained, bp 38° (15 mm), 60° (56 mm); n_D^{20} 1.3183. IR spectrum (ν_{max}, cm^{-1}): 1673 m, 2920 m, 2985 s, 3005 s, 3320 w, 3480 w. PMR spectrum: 3.53 (CH_3; 3H); 4.35 (CH heptet, J 7.7 Hz; 2H).

With Aniline. To 3 g of (VIII) in 10 ml of Freon 113 was added 0.9 g of aniline in 10 ml of absolute ether; the mixture allowed to stand 1 h at −78° and 1 day at 20°. The solvents were stripped and the residue was distilled. Compound (XVIIIb) (3 g, 77%) was obtained, bp 68° (6 mm), mp 30°; n_D^{20} 1.3922. Found %: C 38.5; H 1.83; F 55.7; N 3.46. $C_{13}F_{12}H_7N$. Calculated %: C 38.5; H 1.73; F 56.2; N 3.46. IR spectrum (ν_{max}, cm^{-1}): 1480 w, 1587 w, 1638 m. PMR spectrum: 4.38 (CH heptet, J 7.3 Hz; 1.85 H); 6.45-7.50 (C_6H_5; 5 H).

With Triethylamine. Triethylamine (6.12 g) and 18.9 g of (VIII) were heated for 6 h at 65° in a sealed ampule. After a day, everything was distilled which came over at 100°, and the distillate was washed with conc. HCl, $NaHCO_3$ and water; it was then dried and distilled. Compound (XXI) (6.23 g, 33%) was obtained, bp 68-70°, $n_D^{20} < 1.30$. Found %: C 26.9; H 0.62; F 72.7. $C_7F_{12}H_2$. Calculated %: C 26.7; H 0.64; F 72.7. IR spectrum (ν_{max}, cm^{-1}): 1705 (C=C) s, 3030 and 3050 (CH) m. PMR spectrum: 4.26 (doublet =CH heptet, $J_{(HF)}$ 6.8 Hz; $J_{(HH)}$ 11.1 Hz); 6.62 (doublet =CH, J 11.1 Hz). F^{19} NMR spectrum: 63.0 and 70.2 (broadened quartet and quartet of CF_3C= groups, $J_{F-F)}$ 7.22 Hz), 70.8 [doublet $J_{(H-F)}$ 8.04 of quartets $J_{(F-F)}$ 1.6 Hz from $(CF_3)_2CH$ group]. The residue was distilled under vacuum. There was obtained 7.81 g (32%) of compound (XXII), bp 67-69° (0.05 mm). Found %: C 38.3; H 3.40; F 53.6; N 3.60. $C_{13}F_{12}H_{13}N$. Calculated %: C 38.0; H 3.16; F 55.5; N 3.40. IR spectrum (ν_{max}, cm^{-1}): 1533 s and 1618 s (C=C). PMR spectrum: 1.40 and 3.52 (triplet and quartet of C_2H_5 group, J 7.3 Hz); 5.15 and 7.05 (AB quartet of CH=CH, J 12.2 Hz), 4.40 (CH heptet, J 7.9 Hz).

With Hydrogen Sulfide. A mixture of 4.5 g of (VIII), 0.83 g of NaSH, 2 ml of liquid anhydrous hydrogen sulfide and 10 ml of sulfolane was carefully warmed to 0°, and when homogeneity had been attained, the mixture was rapidly cooled again to −78° and allowed to stand for 3 h. After three days at 0° the excess H_2S was removed and all the material which distilled at 100 (10 mm) was distilled into a trap at −78°. There was obtained 3.08 g (68%) of compound (XXI), which was identical by PMR spectrum and g.c. on column D with that obtained in the preceding experiment.

A homogeneous solution of 2 g of (VIII) in 2 ml of liquid anhydrous H_2S was heated for 20 h at 100°. On distillation, 1.7 g of starting (VIII) was obtained (g.c. on column D). The compound (VIII) was converted into (XV) by treatment with methanol.

Similarly, the absence of a reaction between (VIII) and H_2S in the presence of one molar equivalent of NaSH in dioxane or without the dioxane was ascertained, plus the absence of reaction between (VIII) and sulfolane at 100°.

With Water. A mixture of 3.67 g of (VIII), 4 volumes of dioxane and 0.4 ml of water was shaken in a sealed ampule for 30 min, until it became homogeneous. After 3 h it was diluted with water, the lower layer was separated and it was distilled from an equal volume of concentrated sulfuric acid. After repeated distillation, 3.4 g (82%) of (X) was obtained, identical by g.c. on column B to that obtained from dimer (IIa) and water.

With Butadiene or Ethyl Mercaptan or Thiophenol. Compound (VIII) (4 g) was heated for 40 h at 100° with an equimolecular amount of butadiene, ethyl mercaptan or thiophenol. The absence of reaction was established from the isolation of 3.8-4 g of starting compound (VIII).

Reaction of Methylimine (XVIIIa) with Methylamine. A mixture of 3 g of (XVIIIa) and 0.27 g of methylamine in 5 ml of absolute ether was allowed to stand for 2 days at 20°. After stripping off the solvent, 2.8 g of starting (XVIIIa) was obtained (g.c. on columns A and B, bp 52-53° at 47 mm).

CONCLUSIONS

1. Dimerization of bis(trifluoromethyl)ketene under the action of weak bases leads to a β-lactone dimer.

2. A new reaction of bis(trifluoromethyl)ketene with triethyl phosphite which leads to tetrakis(trifluoromethyl)allene has been studied.

3. An unusual case of facile hydrogenation of tetrakis(trifluoromethyl)allene by triethylamine has been discovered.

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