ALIPHATIC FLUORO DIAZO COMPOUNDS

COMMUNICATION 2. PERFLUORO(a-DIAZO KETONES)

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B. L. Dyatkin and E. P. Mochalina

Institute of Heteroorganic Compounds, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1035-1039, June, 1965 Original article submitted May 24, 1965

The chemistry of α -diazo ketones has been developed greatly in connection with investigations on the Wolff rearrangement and the Arndt-Eistert reaction. This field is attracting attention at present as a result of the great interest in the chemistry of carbenes. It is known that the intermediate particles in these and many other transformations of α -diazo ketones are keto carbenes. In the α -diazo ketone series compounds containing polyhaloalkyl groups have been prepared and investigated. Such substances are of both preparative and theoretical interest. They can serve as starting substances for the preparation of polyhalo compounds of other classes. Moreover, the presence of powerful electron-accepting polychloro- and, particularly, polyfluoro-alkyl groups has a very marked effect on such properties as the thermal and chemical stability of the molecule, the stability of intermediately formed radicals or ions, the course of their further chemical transformations, which are usually more unequivocal than in other cases, etc.

The first polyhalo diazo ketone 1,1,1-trichloro-3-diazoacetone was prepared in 1949 [1, 2] by the action of trichloroacetyl chloride on diazomethane. It was shown that the reaction of this diazo ketone with hydrogen chloride leads to 1,1,1,3-tetrachloroacetone, which by alkaline hydrolysis gives chloroform and glycolic acid and by the action of sulfuric acid gives the ketol 1,1,1-trichloro-3-hydroxyacetone, which rearranges with liberation of hydrogen chloride into 3,3-dichloropyruvaldehyde.



Later, other workers succeeded in isolating the ketol CCl_3COCH_2OH [3]. However, attempts to carry out the Wolff rearrangement under the usual conditions of the Arndt-Eistert reaction were unsuccessful.

In chemical properties 1,1,1-trichloro-3-diazoacetone is close to 3,4,4-trichloro-1-diazo-3-buten-2-one, which was prepared by Roedig and Maier by the action of trichloroacryloyl chloride on diazomethane [4]. This diazo ketone forms halomethyl ketones and dihalomethyl ketones on treatment with hydrogen halides and halogens, respectively, and it forms the acetoxymethyl ketone on treatment with acetic acid.



As the authors point out, for this diazo ketone the Wolff rearrangement cannot be brought about because, like other trichloroacrylic derivatives, it is sensitive to bases. In 1953, by the action of diazomethane on trifluoroacetyl chloride Brown and Musgrave obtained 3-diazo-1,1,1-trifluoroacetone and showed that it undergoes Wolff rearrangement when treated with silver oxide in presence of alcohol, ammonia, or amines with formation of the corresponding 3,3,3-trifluoropropionic acid derivatives [5]:

$\mathbf{CF_3COCHN_2} \xrightarrow{\operatorname{Ag_2O, \ C_2H_5OH}} \mathbf{CF_3CH_2COOC_2H_5}$

They also succeeded in bringing about the rearrangement for 1,1,1-trichloro-3-diazoacetone. By the action of silver oxide in alcohol they obtained a good yield of 3,3,3-trichloropropionic ester; however, attempts to carry out the reaction in presence of ammonia or amides led to the corresponding amides in negligible yields. It is probable that the failures of previous investigators are actually explained by the fact that the rearrangement was conducted in an alkaline medium. Weygand et al. [6] showed that the ultraviolet irradiation of 3-diazo-1,1,1-trifluoroacetone in aqueous dioxane gives 3,3,3-trifluoropropionic acid. This method of bringing about the rearrangement of diazo ketones was discovered by Horner and co-workers [7]. Weygand [6, 8] also obtained 2-diazo-4,4,4-trifluoroacetoacetic ester:

$$(CF_{3}CO)_{2}O + N_{2}CHCOOC_{2}H_{5} \longrightarrow CF_{3}COCN_{2}COOC_{2}H_{5}$$

On irradiation, this appears to decompose with the elimination of nitrogen, but the keto carbone formed $CF_3COCCOOC_2H_5$ is not converted into the ketene

$$0 = C = C \begin{pmatrix} CF_3 \\ COOC_2H_5 \end{pmatrix}$$

but reacts with all the solvents studied. For example, it dehydrogenates alcohols to aldehydes and is itself converted into 4,4,4-trifluoroacetoacetic ester:

$$CF_3COCN_2COOC_2H_5 + C_2H_5OH \xrightarrow{h\nu} CF_3COCH_2COOC_2H_5 + CH_3CHO$$

Thus, the replacement of hydrogen by the electron-accepting ethoxycarbonyl group lowers the tendency of the carbene to undergo rearrangement.

Since only α -diazo ketones with H or COOC₂H₅ on the carbon carrying the diazo group have been described in the literature up to now, we considered it to be of interest to prepare and investigate the properties of fully fluorinated diazo ketones of type R_fCOCN₂R_f. We found that such compounds are formed in good yields by the reaction of perfluoro carboxylic anhydrides with 2-diazo-1,1,1-trifluoroethane:

$$(R_{f}CO)_{2}O + CF_{3}CHN_{2} \longrightarrow R_{f}COCN_{2}CF_{3} + R_{f}COOCH_{2}CF_{3}$$
$$R_{f} = CF_{3}, C_{3}F_{7}, CF_{2}CI$$

Perfluoro(α -diazo ketones) may also be prepared by the action of 2-diazo-1,1,1-trifluoroethane on perfluoro carboxylic acid chlorides, but this method is less convenient because of the low boiling points of the acid chlorides and the difficulty of purifying them from hydrogen chloride and the original acids. It should be noted that with carboxylic acid chlorides, for example acetyl chloride, 2-diazo-1,1,1-trifluoroethane does not react. This is a result of the smaller positive charge of the carbon atom of the carbonyl group of carboxylic acid chlorides and an-hydrides as compared with the corresponding derivatives of perfluoro carboxylic acids.

The perfluoro(α -diazo ketones) which we obtained are mobile yellow liquids, which distill without decomposition at atmospheric pressure; when strongly overheated they decompose explosively. At room temperature they can be kept for an extremely long time. The infrared spectra of these compounds contain absorption bands due to the carbonyl group at 1700-1720 cm⁻¹ and to the diazo group at 2140 cm⁻¹. We did not find the molecular refraction increment of the diazo group in the literature, and we calculated it as the mean of three values-8.95, 8.97, and 9.07-obtained experimentally for perfluoro(α -diazo ketones). This value is 9.00, and we assumed this as the theoretical value.

Some chemical properties of perfluoro(α -diazo ketones) were investigated for use case of 3-diazohexafluoro-2-butanone. This compound does not react with nitrogen dioxide at room temperature, even under ultraviolet irradiation. The latter fact evidences the stability of perfluoro(α -diazo ketones) to irradiation, for under such treatment no liberation of nitrogen is observed. With bromine at room temperature the substance also does not react, but on irradiation nitrogen is liberated and bromine is absorbed with formation of 3,3-dibromohexafluoro-2-butanone;

$$CF_3COCN_2CF_3 + Br_2 \xrightarrow[-N_2]{h\nu} CF_3COCBr_2CF_3$$

The role of the irradiation appears to lie in the activation of the bromine. The liberation of nitrogen also occurs under the action of concentrated sulfuric acid. The substance formed corresponds in analysis to the expected hydroxy ketone $CF_3COCH(OH)CF_3$, but it has an anomalously high b. p. of 76-77° (18 mm) and approximately double the molecular weight (determined cryoscopically in benzene). Under the action of strong alkali the diazo ketone undergoes haloform breakdown with formation of 2-diazo-1,1,1-trifluoroethane and trifluoroacetic acid:

$$CF_3COCN_2CF_3 + NaOH \rightarrow CF_3CHN_2 + CF_3COONa$$

The elimination of 2-diazo-1,1,1-trifluoroethane indicates the high electronegativity of the CF_3CN_2 group in comparison with the CF_3 group.

Since 3-diazohexafluoro-2-butanone was found to be stable to ultraviolet irradiation, we made attempts to prepare the keto carbene CF_3COCCF_3 in other ways. It was found that treatment of the diazo ketone with copper powder leads to decomposition with liberation of nitrogen, but the expected doubled keto carbene $[CF_3COC(CF_3)=]_2$ was not obtained. We then investigated the pyrolysis of 3-diazohexafluoro-2-butanone. The first attempts to effect the pyrolysis of the pure diazo ketone always resulted in explosions. However, we succeeded in conducting the reaction smoothly by diluting the diazo ketone with compound which was inert under the pyrolysis conditions. An example of such a substance is 2,2,2-trifluoroethyl trifluoroacetate. The pyrolysis was brought about by leading a mixture of the vapors of the diazo ketone and this ester into contact with a platinum wire heated to 300° (in a ketene lamp). Nitrogen was then liberated, and the keto carbene formed was isomerized into bistrifluoromethylketene, identified in the form of 3,3,3-trifluoro-2-(trifluoromethyl)propionanilide:

 $CF_3COCN_2CF_3 \xrightarrow{300^\circ} CF_3COCCF_3 \rightarrow (CF_3)_2C = C = O \xrightarrow{C_6H_5NH_2} (CF_3)_2CHCONHC_6H_5$

EXPERIMENTAL

<u>3-Diazohexafluoro-2-butanone.</u> 6.3 g of 2-diazo-1,1,1-trifluoroethane [9] was introduced into a 10-ml twonecked flask, cooled to -30° , provided with a dropping funnel and a reflux condenser, cooled to -78° , and 6.0 g of trifluoroacetic anhydride was added gradually. The temperature of the mixture was brought up to that of the room (by then the liberation of nitrogen had almost stopped), and the mixture was left overnight. 2,2,2-Trifluoroethyl trifluoroacetate (5.1 g, b. p. 55.5-56.5°) was then distilled off through a column of approximately 17-plate efficiency, and the residue was distilled through a short column. We obtained 4.8 g (81.5%) of 3-diazohexafluoro-2-butanone, b. p. 83-85°. After redistillation: b. p. 84.5-85.0°; n_D^{20} 1.3488; d_4^{20} 1.5642. Found: C 23.41; 23.43; F 55.29; 55.05%; MR 28.27. C₄F₆ON₂. Calculated: C 23.48; F 55.31%; MR 28.32.

<u>2-Diazodecafluoro-3-hexanone.</u> This was prepared similarly from 5.4 g of 2-diazo-1,1,1-trifluoroethane and 8.9 g of heptafluorobutyric anhydride. Yield 4.2 g (61.5%), b. p. 109-112°. After redistillation: b. p. 109-110°; n_D^{20} 1.3380; d_4^{20} 1.6712. Found: C 23.57; 23.73; F 62.11; 62.80%; MR 38.19. C₆F₁₀ON₂. Calculated: C 23.55; F 62.09%; MR 38.12.

<u>1-Chloro-3-diazopentafluoro-2-butanone</u>. This was prepared similarly from 5.0 g of 2-diazo-1,1,1-trifluoroethane and 5.5 g of chlorodifluoroacetic anhydride. Yield 3.5 g (69.5%) b.p. 106-110°. After redistillation: b.p. 107.5-108.5°; n_D^{20} 1.3839; d_4^{20} 1.5752. Found: C 21.92; 21.60; F 43.36; 43.80%; MR 33.02. C₄F₅ON₂CL. Calculated: C 21.59; F 42.69%; MR 33.06.

Chlorodifluoroacetic anhydride was prepared by the usual method -by the action of phosphoric anhydride on chlorodifluoroacetic acid; b. p. 93.5-94°; n_D^{20} 1.3500. Found: C 20.13; 20.35; F 29.91; 30.07%. C₄F₄O₃Cl₂. Calculated; C 19.77; F 31.27%.

<u>3,3-Dibromohexafluoro-2-butanone</u>. A mixture of 5.2 g of 3-diazohexafluoro-2-butanone and 1.5 ml of bromine was introduced into a 10-ml quartz test tube fitted with a reflux condenser cooled to -78° and was irradiated with a mercury lamp for 3 h. In the course of this time the theoretical amount of nitrogen was liberated. The mixture was washed with sodium bisulfite solution and water, dried with magnesium sulfate, and distilled. We obtained 4.5 g (53%) of 3,3-dibromohexafluoro-2-butanone, b. p. 97-106°. After redistillation: b. p. 102-103°; n_D^{20} 1.3828; d_4^{20} 2.1402. Found: C 14.44; 14.51; F 33.52; 33.67%; MR 36.81. C₄F₆OBr₂. Calculated: C 14.22; F 33.74%; MR 37.05.

Haloform Breakdown of 3-Diazohexafluoro-2-butanone. 4.3 g of the diazo ketone was introduced into a 10ml two-necked flask fitted with a dropping funnel and a small reflux condenser connected to a trap cooled to -78° , and 40% sodium hydroxide solution was added cautiously dropwise at room temperature until no more gas was liberated. In the trap there condensed 1.8 g (78.5%) of 2-diazo-1,1,1-trifluoroethane, identified in the formation of its addition product with methyl acrylate. The melting point of the substance, alone and in admixture with a known sample [10], was 109-109.5°.

Pyrolysis and Wolff Rearrangement of 3-Diazohexafluoro-2-butanone. A mixture of 1.69 g of 3-diazohexafluoro-2-butanone and 2.15 g of 2,2,2-trifluoroethyl trifluoroacetate was introduced into a ketene lamp fitted with a small reflux condenser connected to a wash bottle and further to a gas buret. The mixture was boiled for a short time to displace air from the lamp, and the lamp was then switched on and the temperature of the spiral was gradually brought to 300°. The pyrolysis of the diazo ketone started, as was indicated by the liberation of nitrogen. It continued for 2.5 h. The ethereal solution through which the gas liberated was bubbled was washed free from excess of aniline with dilute hydrochloric acid and was then washed with water; ether was evaporated. We obtained 1.65 g (75%) of 3,3,3-trifluoro-2-(trifluoromethyl)propionanilide, which after crystallization from benzene had m. p. 168-169°. A mixture with a known sample having the same melting point [11] melted without depression. Regarding the synthesis of (CF₃)₂C=C=O see [12].

SUMMARY

1. By the action of 2-diazo-1,1,1-trifluoroethane on perfluoro carboxylic anhydrides a number of perfluoro- $(\alpha$ -diazo ketones) were obtained.

2. With the case of 3-diazohexafluoro-2-butanone as example, some chemical properties of perfluoro(α -diazo ketones) were investigated. The pyrolysis of 3-diazohexafluoro-2-butanone is accompanied by Wolff rearrangement and leads to bistrifluoromethylketene.

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