

Table 1. Yields and data of nitro diketones (4) and the five-membered ring derivatives (5) to (7).

Product [Reaction variant]	Yield [a] [%]	Physical or spectroscopic data
(4a), R = C ₂ H ₅ , R' = CH ₃	80	b.p. 180°C/3 torr [b]
(4b), R-R' = -(CH ₂) ₄ -	65	m.p. 47–48°C
(4c), R-R' = -(CH ₂) ₅ -	73	m.p. 70–73°C
(4d), R-R' = -(CH ₂) ₆ -	69	m.p. 53–54°C
(4e), R-R' = -(CH ₂) ₁₀ -	75	m.p. 119°C
(4a) → (7a) [Var. B, 15 h]	35	¹ H-NMR: α-hydroxy-CH, δ = 4.9 ppm (m)
(4b) → (6b) [Var. A]	42	¹ H-NMR: vinyl-H, δ = 6.10 and 7.52 ppm
(4b) → (7b) [Var. B, 12.5 h]	31	¹ H-NMR: OH, δ = 4.4 (br. s), α-hydroxy-CH, 4.8 ppm (m)
(4c) → (6c) [Var. A]	67	m.p. 68.8–70.2°C [c]
(4c) → (6c) [Var. B, 2.3 h] [d]	88	m.p. 68–70°C
(4c) → (7c) [Var. B, 18 h] [d]	60	b.p. 180°C/8 torr [b]
(4d) → (6d) [Var. A]	16	b.p. 160°C/0.01 torr [b]
(4e) → (5e) [Var. A]	38	m.p. 155–156°C

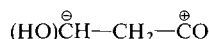
[a] Only acylation to give (4c) and its cyclization have so far been optimized.

[b] Bath temperature on molecular distillation.

[c] Ca. 90% diastereomer, separated by chromatography.

[d] See experimental.

by two geminal H atoms). As shown by the newly formed bonds emphasized by bold print in formula (7), β-nitropropionyl chloride represents the synthetic building block



None of the numerous other methods known for the construction of five-membered rings according to a (C₃ + C₂) pattern gives derivatives having the same functionality as the above sequence of two readily executed steps. The cyclization step requires further optimization. Syntheses of jasmonoids, rethronoids, prostanoids, and other natural products containing five-membered rings are currently under investigation.

Procedure

3a-Hydroxy-4,5,6,7,8,8a-hexahydroazulen-1(3aH)-one (6c) and 3-hydroxy-3,4,5,6,7,8-hexahydroazulen-1(2H)-one (7c) from 2-(3-nitropropionyl)-1-cycloheptanone (4c): A mixture of (4c) (2.13 g), diisopropylamine (3.1 ml), THF (80 ml), *n*-hexane (13 ml), and hydrochloric acid/borate buffer solution (200 ml, pH = 8) is vigorously stirred at room temperature for 2.3 h and then acidified with 10% aqueous acetic acid. The mixture is extracted three times with CH₂Cl₂, the organic phases are washed with 2.5% NaHCO₃ and H₂O, and dried over Na₂SO₄; 1.69 g of crude product is obtained on stripping off the solvent. Chromatography (SiO₂, ether/CCl₄ 4:1) affords 1.46 g (88%) of (6c), m.p. 68–70°C (from CHCl₃/C₆H₁₄). Reaction for 18 h under otherwise identical conditions (including work-up and purification) gives 0.99 g (60%) of (7c) as an oil, b.p. 180°C bath temperature/8 torr.

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CAS Registry numbers:

(1a), 107-87-9; (1b), 108-94-1; (1c), 502-42-1; (1d), 502-49-8; (1e), 830-13-7; (4a), 62250-63-9; (4b), 62250-64-0; (4c), 62250-65-1; (4d), 62250-66-2; (4e), 62250-67-3; (5e), 62250-68-4; (6b), 62250-69-5; (6c), 62250-70-8; (6d), 62250-71-9; (7a), 62250-72-0; (7b), 62250-73-1; (7c), 62250-74-2; β-nitropropionyl chloride, 51834-15-2

[1] D. Seebach, V. Ehrig, Angew. Chem. 86, 446 (1974); Angew. Chem. Int. Ed. Engl. 13, 400 (1974); Chem. Ber. 108, 1961 (1975).

[2] From commercially available (Aldrich) β-nitropropionic acid and thionyl chloride in the presence of a trace of DMF; 75% yield; b.p. 78°C/4 torr [G. Barger, F. Tutin, Biochem. J. 12, 405 (1918)].

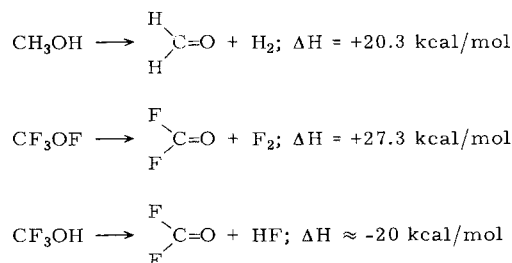
[3] For execution of this general 1:1 reaction of enolates with acyl chlorides, see: A. K. Beck, M. S. Hoekstra, D. Seebach, Tetrahedron Lett. 1977, 1187.

[4] Cf. G. Stork, C. Kowalski, G. Garcia, J. Am. Chem. Soc. 97, 3258 (1975); T. Shono, Y. Matsumura, H. Hamaguchi, K. Nakamura, Chem. Lett. 1976, 1249; G. Piancatelli, A. Scettri, Synthesis 1977, 116.

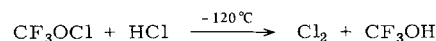
Trifluoromethanol, CF₃OH^[**]

By Konrad Seppelt^[*]

Very little is known about perfluorinated alcohols, except (CF₃)₃COH and *c*-(CF₂)₃CFOH^[1]. The reason for this is that primary and secondary perfluoroalcohols generally eliminate hydrogen fluoride with formation of carbonyl compounds. Methanol is stable towards hydrogen elimination, just as trifluoromethyl oxyfluoride is stable towards fluorine elimination^[2]; but, as expected, the simplest perfluoroalcohol, CF₃OH, is unstable towards HF cleavage.



It has now been possible, however, to isolate this compound as a product of the reaction of trifluoromethyl oxychloride with hydrogen chloride.



The reaction principle is recombination of partially positively charged and partially negatively charged chlorine. The reaction temperature must be kept as low as possible, an inert solvent, *e.g.* CF₃Cl, being employed to take up the

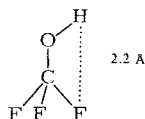
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heat of reaction. Excess HCl as well as CF₃Cl and Cl₂ can be pumped off completely at -110°C.

The colorless trifluoromethanol melts at -82°C and has an extrapolated boiling point of -20°C. It was characterized by nuclear magnetic resonance spectra (¹H: singlet at δ=8.65 ppm vs. TMS; ¹⁹F: singlet at δ=+54.5 ppm vs. CFCl₃; ¹³C: quartet at δ=+118 ppm vs. TMS, J_{CF}=256 Hz), mass spectrum (m/e=86, CF₃OH⁺), IR vapor phase spectrum 3675 (PQR, νOH), 1401, 1364, 1283, 1187, 1117 cm⁻¹ and by controlled decomposition to CF₂O and HF at room temperature.

Although the decomposition of CF₃OH is thermodynamically much more strongly favored than that of the recently prepared HOSF₅^[3], the alcohol is more stable; it decomposes slowly at -20°C, while HOSF₅ already starts to decompose at -60°C. This kinetic effect can be explained in terms of the larger intramolecular H...F distance, which has been estimated to be 2.2 Å in CF₃OH, and 1.9 Å in HOSF₅.



Because of this distance no intramolecular H...F bridge is observed in the IR vapor phase spectrum. Intermolecular bridges can be ruled out on the basis of the high vapor pressure of the alcohol: the boiling point of CF₃OH is about 85°C lower than that of CH₃OH. A further explanation for the relative stability of CF₃OH can be that the HF elimination is not allowed as a synchronous reaction. In the case of HOSF₅ this can be cancelled on account of the d orbitals.

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CAS Registry numbers:

CF₃OH, 1493-11-4; trifluoromethyl oxychloride, 22082-78-6

- [1] S. Andreades, D. C. England, J. Am. Chem. Soc. 83, 4670 (1961).
[2] R. S. Porter, G. H. Cady, J. Am. Chem. Soc. 79, 5628 (1957).
[3] K. Seppelt, Angew. Chem. 88, 56 (1976); Angew. Chem. Int. Ed. Engl. 15, 44 (1976); Z. Anorg. Allg. Chem. 428, 35 (1977).

Cyclopropenes as Vinylcarbenoids: Intermolecular Carbene-Addition Reactions of Sulfinyl- and Sulfonylcyclopropenes at Room Temperature^[**]

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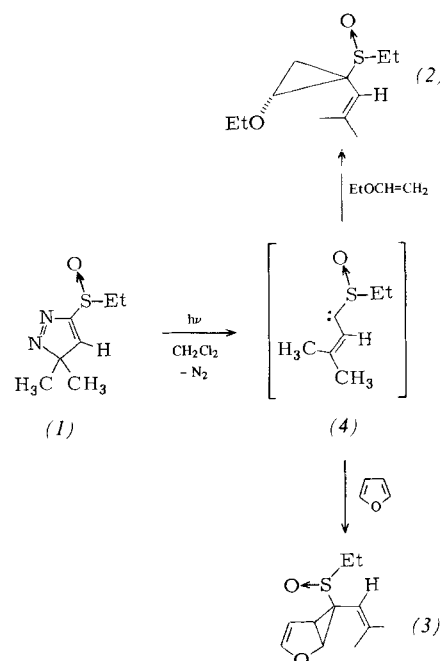
The interrelation between vinylethylene^[1] and vinylcarbenes^[2] on the one hand and cyclopropenes on the other has been the subject of numerous studies in recent years. In particular, the thermolytic (>150°C) or photolytic ring-opening of cyclopropenes would appear to proceed *via* vinylcarbenes^[3], which, however, are usually stabilized by intramolecular reactions.

We have now been able to demonstrate an isomerization of sulfinyl- and sulfonylcyclopropenes to the corresponding vinylcarbenes and found that the carbene forms react as intermolecular cycloaddition partners with nucleophilic olefins.

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Irradiation^[4] of the sulfinyl-3*H*-pyrazole (1)^[5] in ether or methylene chloride leads to rapid and stoichiometric loss of one mol of nitrogen. After removal of the solvent at room temperature there remains a complex mixture of products. On irradiation in vinyl ether or furan, however, the products (2) and (3), respectively, are formed smoothly and stereospecifically.



Compound (2) is isolated in the form of its *E-Z* isomers in 75% yield^[6]. IR and NMR spectra of the liquid product are consistent with the proposed structure^[7]. The *trans*-divinylcyclopropane compound (3) (m.p. 76°C, colorless) can be isolated in 95% yield^[6]. It remains unchanged on heating for two hours at 90°C. Its IR and NMR spectra are in agreement with the given structure^[7]. The NMR spectrum contains, in particular, the signals characteristic for similar dihydrofuran derivatives^[8].

Apparently, photolysis of 3*H*-pyrazole (1) leads to formation of the carbene (4) which in the absence of reactive cycloaddition partners ought to cyclize to a cyclopropene.

In order to check this with the aid of a Diels-Alder trapping reaction the 3*H*-pyrazole (1) was irradiated in methylene chloride at -25°C until complete extrusion of nitrogen, the UV irradiation switched off, and the irradiated solution immediately treated with cyclopentadiene. After several hours' standing at 5°C and removal of solvent, however, no Diels-Alder adduct of a cyclopropene was detectable, but only polymers along with the carbene addition product (5) [*trans*-divinylcyclopropane structure, stability, compatible IR and NMR spectra], which could be isolated pure in ca. 30% yield^[6]. If the same experiment is carried out with furan instead of cyclopentadiene again only the carbene addition product (3) is formed, and in almost the same yield as in the irradiation in furan.

