^{18}O enrichment was calculated by taking one-half the height of the mass 46 peak times 100 and dividing this result by the sum of the heights of the mass 44 peak and mass 46 peak. The value obtained from the blank sample was subtracted from the value for the enriched sample to compensate for the natural abundance of ^{18}O. Duplicate analyses of the same compounds showed that the analytical procedure was accurate to ±3%.

Registry No.—**2a**, 18888-64-7; **2a**-*carbonyl*-^{18}O, 18893-96-4; **2b**, 18887-40-6; **2c**, 16544-65-3; **2c**-*carbonyl*-^{18}O, 18893-97-5; **2d**, 18887-42-8; **2e**, 18887-43-9; **2f**, 18887-44-0; **2g**, 18887-43-9; **2h**, 18887-46-2; **2i**, 18887-47-3; **2i**-*carbonyl*-^{18}O, 18893-98-6; **2j**, 38887-48-4; **4a**, 18893-99-7; **4c**, 18894-00-3; **4i**, 18902-55-1; **5a**, 18894-01-4; **5c**, 18894-02-5; **5i**, 18894-03-6.

Acknowledgments.—The authors are most grateful to Mr. Gary Weber for performing the mass spectral analyses, to Professor Marvin Charton for several helpful discussions, to the Arizona State University Grants Committee for financial support and two summer stipends for K. B. G., and to the Garrett Corp. and Arizona State University for use of their computer facilities.

Notes

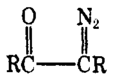
Cycloadditions. XXIV. Cycloadducts from Arylaroyldiazomethanes and Carbon Disulfide[1,2]

John E. Baldwin[3] and Jon A. Kapecki[4]

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

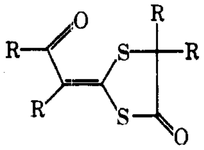
Received July 2, 1968

A reinvestigation of the adduct derived from azibenzil (**1a**) and carbon disulfide[5] led Yates and Christensen[6] to assign it structure **2a** (or its geometrical isomer). A supposedly analogous adduct obtained from the reaction of 3-diazobutanone (**1b**) and carbon disulfide was represented by formula **2b**,[7] but a recent X-ray single-crystal structure analysis on this adduct established **3b** as an accurate structural assignment.[8,9]

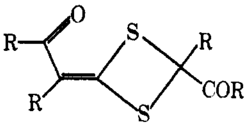


$R\overset{O}{\overset{\|}{C}}-\overset{N_2}{\overset{\|}{C}}R$

1



2



3

a, $R = C_6H_5$
b, $R = CH_3$
c, $R = p\text{-}C_6H_4F$

Whether the adduct from azilbenzil might require a similar structural reassignment (**3a** instead of **2a**) was answered through the present work.

Results and Discussion

Structure **2** has two R groups which would be identical by symmetry, whereas in **3** each of the four R groups is distinct. This factor became the basis for an approach to the structural distinction; the adduct in which R = $p\text{-}C_6H_4F$– (**2c** or **3c**) was synthesized and its fluorine nmr spectrum examined.

p-Fluorophenyl-*p*-fluorobenzoyldiazomethane (**1c**) was synthesized through the sequence *p*-fluorobenzaldehyde → *p,p'*-difluorobenzoin → *p,p'*-difluorobenzil → *p,p'*-difluorobenzil monohydrazone → **1c**. Heating the difluoroazibenzil and carbon disulfide to reflux gave a mixture of products from which the adduct $C_{29}H_{16}F_4O_2S_2$ **2c** or **3c**, mp 145–146°, was isolated by fractional crystallization.

The infrared spectra of this tetrafluoro adduct, mp 145–146°, and of the adduct from azibenzil were identical but for three exceptions. One was the expected[10] strong carbon-fluorine bond absorption at 1162 cm^{-1}. The second was a weak band at 945 cm^{-1} in the tetrafluoro adduct, not observed in its unsubstituted analog. The third difference came in the region 1620–1575 cm^{-1}. The compound assigned structure **2a** shows three medium-intensity peaks at 1620, 1598, and 1578 cm^{-1}. In the tetrafluoro adduct, this region is obscured by a very strong band at 1598 cm^{-1} with a shoulder probably containing a band near 1620 cm^{-1}.

The adduct of mp 145–146° showed three absorptions in a ^{19}F nmr spectrum; they had similar fine structure and a 1:1:2 ratio of relative intensities (Figure 1). In tetrahydrofuran, these absorptions appeared

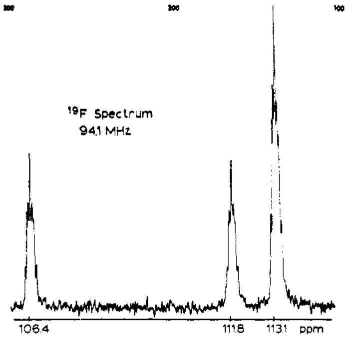


Figure 1.—Fluorine-19 nmr spectrum of adduct **2c**, mp 145–146°, taken as a solution in tetrahydrofuran.

---

[1] Supported in part by Public Health Research Grant GM-14381.

[2] Paper XXIII in this series: J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, in press.

[3] Alfred P. Sloan Research Fellow.

[4] National Science Foundation Predoctoral Trainee, 1965–1968.

[5] J. Meyer, *Helv. Chim. Acta*, **8**, 38 (1925).

[6] P. Yates and B. G. Christensen, *Chem. Ind.* (London), 1441 (1958).

[7] A. J. Kirby, *Tetrahedron*, **22**, 3001 (1966).

[8] J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *Tetrahedron Lett.*, 5307 (1967).

[9] J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Amer. Chem. Soc.*, **90**, 5800 (1968).

[10] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 57.

at 106.4, 111.8, and 113.1 ppm relative to internal fluorotrichloromethane. In bromoform, these peaks came at 105.3, 111.0, and 112.3 ppm, and no broadening of the upfield signal was observed. Fluorine chemical shifts are particularly sensitive to solvent effects;[11,12] the constancy of the 1:1:2 pattern as solvent and chemical shifts change affords some indication that an accidental coincidence of fluorine chemical shifts in two nonidentical p-C_6H_4F groups is not responsible for the spectral results.

The spectroscopic data for the tetrafluoro adduct are consistent with structure **2c**, not with **3c**, and the adduct from azibenzil is accordingly better represented by **2a** than by **3a**. The arylaroyldiazomethanes and carbon disulfide give adducts of structure **2**, while the alkylalkoyldiazomethanes lead to the 2-methylene-1,3-dithiacyclobutanes **3**. Fresh degradative and synthetic results reported by Yates and Williams[13] have independently corroborated structure **2a** for the adduct from azibenzil.

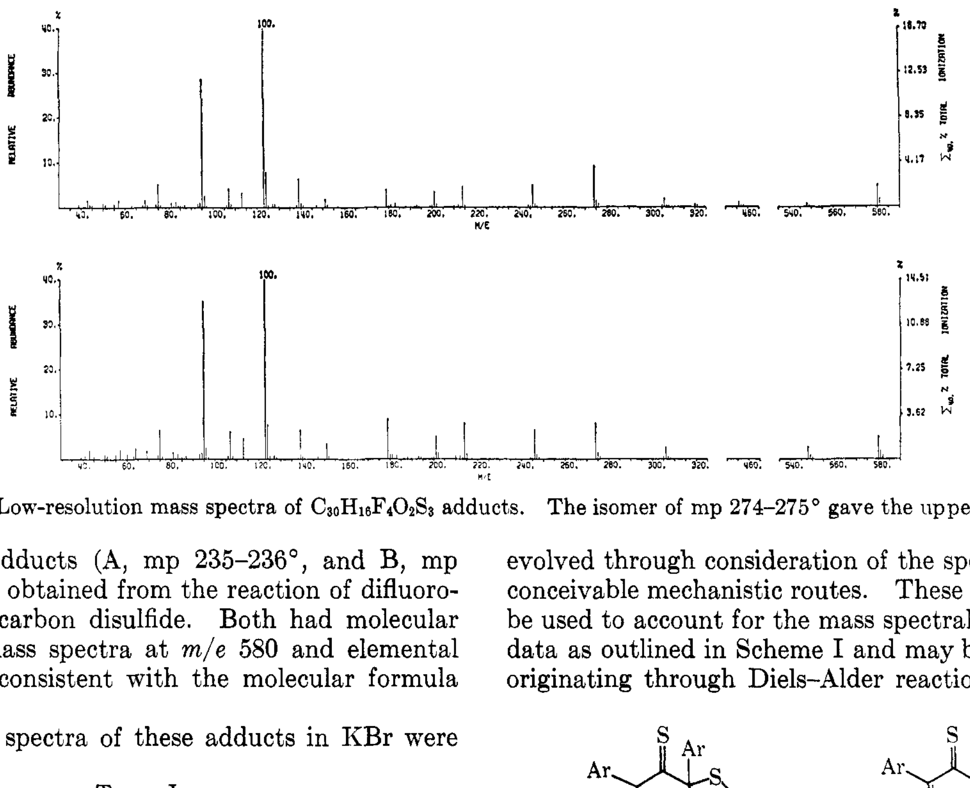


Figure 2.—Low-resolution mass spectra of $C_{30}H_{16}F_4O_2S_3$ adducts. The isomer of mp 274–275° gave the upper spectrum.

Two other adducts (A, mp 235–236°, and B, mp 274–275°) were obtained from the reaction of difluoroazibenzil with carbon disulfide. Both had molecular ions in their mass spectra at m/e 580 and elemental analyses most consistent with the molecular formula $C_{30}H_{16}F_4O_2S_3$.

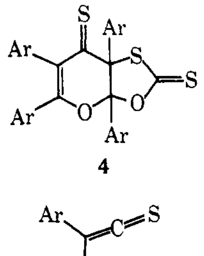
The infrared spectra of these adducts in KBr were very similar to that of adduct **2c**, except for the absence of a strong band at 1710 cm^{-1}. The spectra of A and B were virtually identical except for minor variations: at 1560 and 987 cm^{-1} the high melting isomer B has bands of medium intensity not distinctly present in the other; the relative intensities of doublets at 1095 and 1080 cm^{-1} differ in the two adducts; a band at 900 cm^{-1} appears in the spectrum for B, while A shows a corresponding band at 885 cm^{-1}. Isomer B had $\lambda_{max}^{CH_2Cl_2}$ 267 mμ (ϵ 3.2 × 10^3) and 391 (4.7 × 10^3). Low-resolution mass spectra of the two adducts taken under similar conditions show nearly identical fragmentation patterns (Figure 2). High-resolution mass spectra for adduct A,[14] summarized in Table I, permitted sure assignments of empirical formulas for some peaks. It proved impossible to obtain elemental composition data for the molecular ion at m/e 580. The m/e 581 peak distorted the PFK peak at 581 so that it could not be used as a mass standard line.

TABLE I

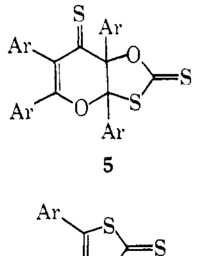
HIGH-RESOLUTION MASS SPECTRAL DATA FOR MAJOR PEAKS IN SPECTRUM OF ADDUCT WITH MP 236°

Molecular formula	m/e Obsd	m/e Calcd	Rel intensity
$C_{30}H_{16}F_4O_2S_2$	548.0523	548.0528	12.3
$C_{15}H_8F_2OS$	274.0254	274.0264	14.2
$C_{14}H_8F_2S$	246.0323	246.0315	6.8
$C_{14}H_8F_2$	214.0592	214.0594	6.8
$C_{13}H_7F_2$	201.0502	201.0516	8.0
C_7H_4FO	123.0272	123.0246	38.2
C_7H_4F	107.0304	107.0297	15.1
C_6H_3	75.0286	75.0235	19.7

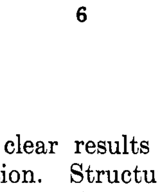
Structure postulates **4** and **5** for these adducts were evolved through consideration of the spectral data and conceivable mechanistic routes. These postulates may be used to account for the mass spectral fragmentation data as outlined in Scheme I and may be envisioned as originating through Diels–Alder reactions of **6** and **7**.



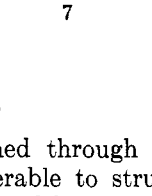
4



5



6



7

Ar = p-C_6H_4F

Conclusions

Two clear results were obtained through this investigation. Structure **2** is preferable to structure **3** for the type of cycloadduct obtained by Meyer[5] from

---

[11] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 76.

[12] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, p 872.

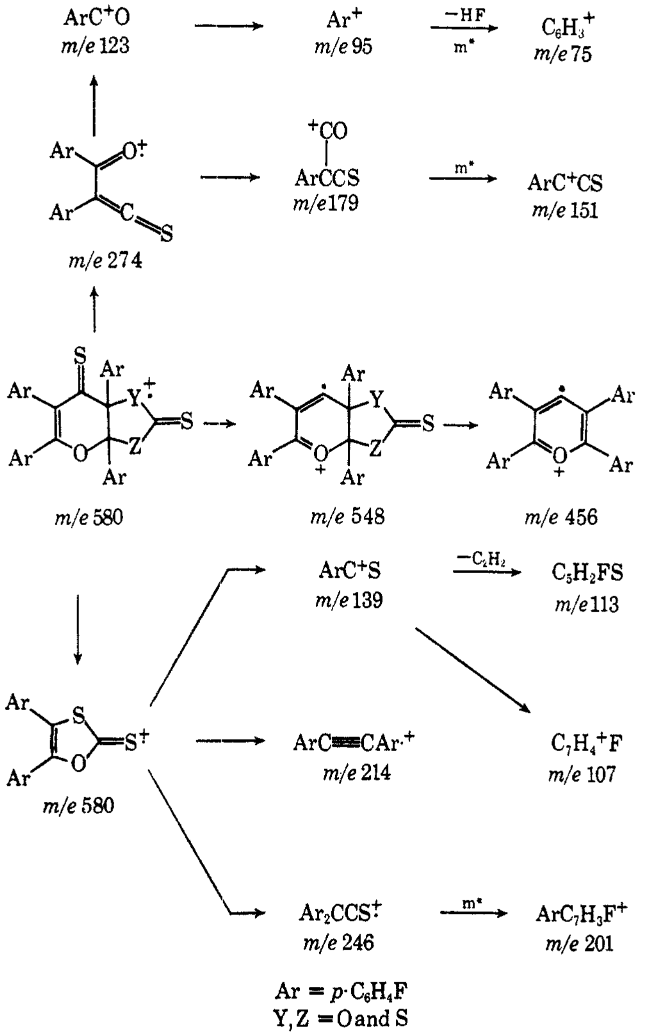
[13] P. Yates and L. L. Williams, *Tetrahedron Lett.*, 1205 (1968).

[14] Obtained through the good offices of Dr. George Van Lear and the Mass Spectrometry Center at Purdue University.

azibenzil and carbon disulfide. Seemingly modest variations in substrate **1**, replacing phenyl with methyl, or phenyl with *p*-fluorophenyl, lead to strikingly different results in reactions with carbon disulfide. The alkylalkoyldiazomethanes give rise to adducts **3**; *p*-fluorophenyl-*p*-fluorobenzoyldiazomethane gives both the expected adduct **2c** and two more complex products $C_{30}H_{16}F_4O_2S_3$. Structural determinations for adducts A and B, and an understanding of how they are formed, will depend upon further experimentation.

SCHEME I

RATIONALIZATION OF MASS SPECTRUM OF $C_{30}H_{16}F_4O_2S_3$ ADDUCTS



Experimental Section

***p,p'*-Difluorobenzil** was prepared in two steps from *p*-fluorobenzaldehyde, according to a procedure described for the conversion of benzaldehyde to benzoin to benzil.[15] *p,p'*-Difluorobenzoin was recrystallized from ethanol and had mp 85–86°.

Anal. Calcd for $C_{14}H_{10}O_2F_2$: C, 67.74; H, 4.06. Found: C, 67.46; H, 4.31.

p,p'-Difluorobenzil was recrystallized from benzene to give yellow needles, mp 119–121° (lit.[16] mp 123–123.5°), in 38% over-all yield.

***p,p'*-Difluorobenzil Monohydrazone.**—*p,p'*-Difluorobenzil (13 g) was converted into the monohydrazone with hydrazine hydrate in ethanol.[17] An 81% yield of fine yellow crystals, mp 183–185°, was obtained. The analytical sample, mp 190–191°, was recrystallized from ethanol.

Anal. Calcd for $C_{14}H_{10}F_2N_2O$: C, 64.63; H, 3.87; N, 10.77. Found: C, 64.33; H, 4.05; N, 10.84.

***p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane** was prepared from 11.1 g of *p,p'*-difluorobenzil monohydrazone through oxidation by mecuric oxide.[18] The crude product (6.8 g) was recrystallized from diethyl ether to give 3.2 g of orange product: mp 102–106° dec; $\bar{\nu}$ ($CHCl_3$) 2080, 1620–1600, 1500, 1340, 1155, 865, and 830 cm^{-1}. Further recrystallizations did not raise the decomposition temperature.

Anal. Calcd for $C_{14}H_8F_2N_2O$: C, 65.13; H, 3.12; N, 10.84. Found: C, 65.23; H, 3.36; N, 10.81.

Reaction of *p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane with Carbon Disulfide.—*p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane (4.4 g, 17 mmol) and 40 ml of carbon disulfide were heated at reflux for 40 hr. The reaction mixture was cooled, filtered, and concentrated. Yellow crystals (4.4 g) were collected, washed with ether, and dried.

The crude product was recrystallized from absolute ethanol to give two crops of yellow crystals, 1.2 and 1.0 g, having mp 90–105°, and a residue insoluble in ethanol (1.2 g of yellow material, mp 267–270°).

The first two crops of crystals were dissolved in hot ethanol and, as the solution was allowed to cool slowly, a flocculent mass of very fine, hairlike yellow needles was obtained. This solid had mp 235–236° after repeated recrystallization from ethanol.

Anal. Calcd for $C_{30}H_{16}F_4O_2S_3$: C, 62.06; H, 2.78. Found: C, 61.43; H, 2.92.

Concentration of the ethanolic mother liquors gave another solid which, after repeated recrystallization from carbon disulfide, had mp 145–146°.

Anal. Calcd for $C_{29}H_{16}O_2S_2$: C, 64.91; H, 3.01; S, 11.95. Found: C, 64.54, 64.58; H, 3.12, 3.15; S, 11.81.

The high-melting residue from the first recrystallization was recrystallized four times from chloroform to obtain lemon yellow plates, mp 274–275° dec.

Anal. Calcd for $C_{30}H_{16}F_4O_2S_3$: C, 62.06; H, 2.78; S, 16.58. Found: C, 61.55; H, 2.98; S, 16.42.

The combined 3.2 g of crops 1, 2, and 3 contained approximately 12% of the adduct of mp 235–236°, 66% of the $C_{29}H_{16}F_4O_2S_2$ adduct, mp 145–146°, and 22% by weight of the high melt-product, mp 274–275°. Spectral data for these three adducts are given in the discussion.

Registry No.—*p,p*-Difluorobenzil monohydrazone, 18598-41-9; **1c**, 18542-79-5; **2c**, 18542-80-8; **4**, 18542-81-9; **5**, 18542-82-0; carbon disulfide, 75-15-0.

---

[15] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 170.

[16] W. Voegtli and P. Läuger, *Helv. Chim. Acta*, **38**, 46 (1955).

(17) *Cf.* L. I. Smith and H. H. Hoehn, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 356.

(18) *Cf.* C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 496.

Lack of Oxygen-18 Scrambling in the Solvolytic Rearrangement of Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate[1a]

WILLIAM G. DAUBEN AND JAMES L. CHITWOOD[1b]

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

Received August 26, 1968

Wagner–Meerwein rearrangements can be considered to fall within two theoretical limits with regard

---

(1) (a) This investigation was supported in part by Grant No. GP 3890, National Science Foundation. (b) National Institutes of Health Predoctoral Fellow, 1966–1968.