small amount of 95% ethanol; the yellow powder which resulted was isolated on a Büchner funnel and air dried. Recrystallization from absolute ethanol–ether afforded 1.9 g (71%) of carbinol ethyl ether III, mp 123–126°, with infrared spectrum superimposable on that of the product prepared by method A.

D. Treatment of Methiodide I with Aqueous Ethanolic Acetic Acid.—A slurry of 1.4 g (2.5 mmoles) of methiodide I[2] was refluxed in a mixture of 15 ml of 95% ethanol and 15 ml of 4% acetic acid. After 24 hr the system was stripped and the residue was extracted with ether. This solution was dried over $MgSO_4$, filtered, and stripped. Without further work-up, III was obtained, mp 123–126°, 0.78 g (81%), with infrared spectrum identical with that of the product prepared by method A.

E. Silver Oxide Method.—The methiodide I (0.57 g, 1 mmole) was dissolved in hot ethanol–water and shaken with excess Ag_2O (0.23 g, 2 mmoles) and filtered (ether wash), and the filtrate was concentrated on a rotary evaporator until an oil began to separate. Solid NaOH was added until a concentration of 50% was obtained. This solution was refluxed until no further trimethylamine was evolved (5 hr). The cooled solution was diluted with water and extracted with ether; the combined extracts were dried over $MgSO_4$. After stripping, 0.22 g (58%) of an orange, crystalline solid was obtained, mp 125–126°, from hexane. Repetition of this procedure on three times the scale described afforded 0.9 g (79%) of III, mp 127–128°, from ethanol, identical in all respects to the material prepared by method A.

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meso- and *dl*-α,α′-Bis(difluoramino)bibenzyls. Preparation and Nuclear Magnetic Resonance Spectra

FREDERIC A. JOHNSON, CAROLYN HANEY, AND
TRAVIS E. STEVENS

Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama

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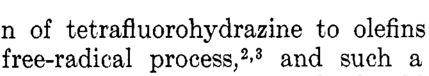
A recent study of the interaction of tetrafluorohydrazine (N_2F_4) and polycyclic aromatic hydrocarbons[1] included the report that *trans*-stilbene produced an α,α′-bis(difluoramino)bibenzyl. This addition compound of stilbene and N_2F_4 was reported to decompose above 80°, and was postulated from its proton nmr spectrum as either a mixture of *meso* and *dl* adducts or one adduct with two conformations.

As part of a study of the properties of organic difluoramino compounds, we have characterized the product from *trans*-stilbene and tetrafluorohydrazine[2] as a mixture of the *meso* and *dl* isomers. The *meso* isomer (Ia) was isolated in 37% yield; the *dl* isomer (Ib) was present in 50% yield.



$$C_6H_5\overset{H}{C}{=}\overset{H}{C}C_6H_5 \longrightarrow C_6H_5\underset{NF_2}{\overset{H}{C}}-\underset{NF_2}{\overset{H}{C}}C_6H_5$$

Ia, mp 158–159°
b, mp 111.5–113°

Addition of tetrafluorohydrazine to olefins appears to be a free-radical process,[2,3] and such a lack of stereospecificity is expected for radical additions to *trans*-stilbene.[4]

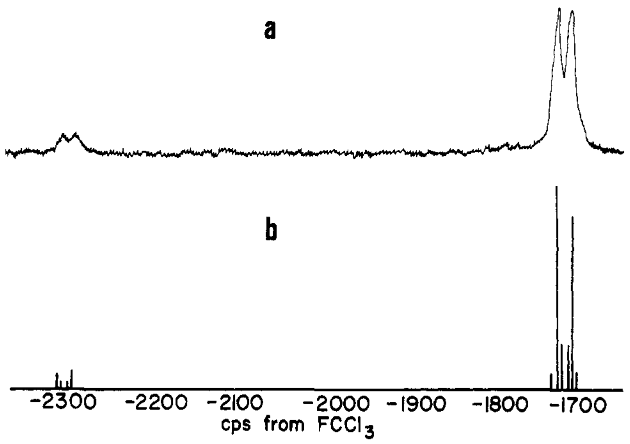


Figure 1.—(a) Observed F^{19} "B" spectrum; (b) calculated F^{19} "B" spectrum.

The nmr spectra of Ia and Ib are deceptively simple—only 18 peaks are apparent in the combined F^{19} and H^1 spectra of the *dl* mixture and even fewer for the *meso*. However, the line widths of the peaks (10–12 cps for F^{19} and 2–4 cps for H^1) make it obvious that these are not single transitions. Several reasons for this situation are discussed below.

Nitrogen coupling is not apparent in these compounds, although it has been observed at room temperature for NF_3, N_2F_4, and the N_2F_2 isomers. The nitrogen nucleus in the bibenzyl compounds is subject to a less symmetric environment, which may be expected to facilitate relaxation of this nucleus through a quadrupole mechanism. Cooling or warming of these compounds might be expected to either increase or decrease the visible effects of nitrogen on the F^{19} and H^1 spectra, but no noticeable changes occurred between −60 and +100°. However, decoupling of N^{14} by irradiation at 3.076 or 2.890 Mc for H^1 and F^{19} spectra, respectively, does cause a slight sharpening of peaks. Thus, while nitrogen (in part) accounts for the rather broad lines observed no spin–spin couplings to nitrogen influence the observed patterns.

The NF_2 groups are bound to optically active carbon atoms. The pyramidal geometry of the NF_2 group causes the two fluorine atoms to be magnetically nonequivalent in a fashion previously described[5] for CH_2 groups in similar environments. Significant shift differences for the two F^{19} nuclei result; acetone is a suitable solvent for the *dl* enantiomers in that it enhances the shift difference. Since each fluorine has a magnetically identical counterpart in the opposite enantiomer, spectra of the enantiomers are identical and indistinguishable. The F^{19} nmr (Figures 1 and 2) has the gross appearance of an ABX system of very large J_{FF} (587 cps) and comparatively small (10 to 30 cps) J_{HF_A} and J_{HF_B}.

The existence of an AB pattern from the C^*-NF_2 system implies that the nitrogen atom is not inverting within the time characteristic of the nmr experiment. For only one nonring compound does this type of behavior appear to have been established[6]—the case of N-benzyl-O,N-dimethylhydroxylamine in the range of −30 to −10°. The AB spectrum of Ib was observed

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[1] H. Cerfontain, *J. Chem. Soc.*, 6602 (1965).

[2] R. C. Petry and J. P. Freeman, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, Abstract S-46.

[3] R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 5912 (1961); A. J. Dijkstra, Ph.D. Thesis, Rotterdam, 1965.

[4] Addition of N_2O_4 to *trans*-stilbene, also a radical process: T. E. Stevens [*J. Am. Chem. Soc.*, **81**, 3593 (1959)] gave 21% *meso*-α,α′-dinitrobibenzyl and 32% *dl*-α,α′-dinitrobibenzyl.

[5] P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **47**, 49 (1961).

[6] D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965).

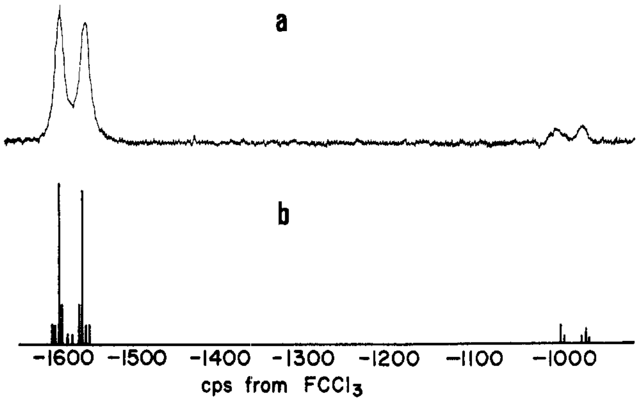


Figure 2.—(a) Observed F^{19} "A" system; (b) calculated F^{19} "A" spectrum.

to persist at 140°; although some decrease in the AB shift was noted, no collapse of the AB pattern occurred.

The two protons of the *dl* isomers while chemically identical and having the same chemical shift by virtue of their identical environments exhibit spin-coupling nonequivalence because of their different relationships to the two NF_2 groups. This spectrum is therefore of the AA'BB'XX' type (Figure 3).

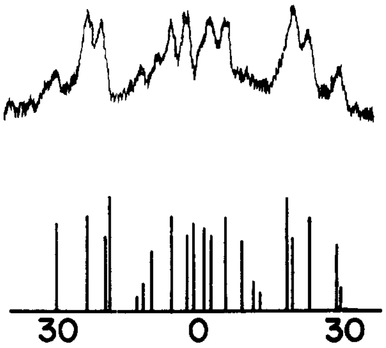


Figure 3.—Experimental and calculated 40-Mc proton spectra.

Approximate parameters were derived by treating the fluorine spectrum as the AB portion of an ABX spectrum. Analogy to CHF systems indicates[7] that the signs of all coupling constants are positive. Spectra were calculated with the Swalen–Reilly program[8] and compared with the observed F^{19} peaks. Experimental and calculated F^{19} spectra are shown in Figures 1 and 2. Some 152 transitions of intensity greater than 0.1 (summed intensity for F^{19} = 126) occur in the calculated spectrum; those occurring within 0.5 cps of one another have been summed to give the line graph of the calculated spectrum. The observed 10-cps line width is accounted for by the spread of transitions about the position indicated by the ABX approximation, and by the neglected small couplings.

In the calculated spectra, the parameters shown in Table I were used. The coupling constants between protons and each fluorine in the "distant" NF_2 group were taken to be 0. While spectra of similar compounds indicate this coupling to be 0–2 cps, the extensive overlapping of lines here prevents observation of these couplings. Hence, although they certainly contribute to the widths of the observed lines, these constants have been taken as 0 for simplicity and economy of calculation. All shifts and coupling constants are believed to be within ±1 cps of the true values.

Table I

Spectral Constants of Ib in Acetone at 40 Mc

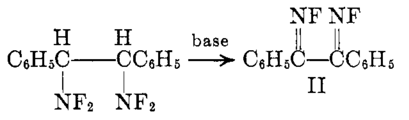
Shifts[a]	Coupling constants, cps			
F_1,F_3 ϕ −46.89	J_{12}, J_{34}	587	J_{56}	10.5
F_2,F_4 ϕ −35.75	J_{13}, J_{23}	0		
H_5,H_6 δ 5.70	J_{14}, J_{24}	0		
	J_{15}, J_{36}	13.8	J_{25}, J_{46}	33.8
	J_{16}, J_{26}	0	J_{35}, J_{45}	0

[a] F^{19} in parts per million relative to $FCCl_3$ as internal standard, 40 Mc; H^1 relative to tetramethylsilane internal standard at 40 Mc.

The spectra of the *meso* diastereoisomer are similar in interpretation. The general features of NF_2 on optically active carbons remain. While each fluorine is now identical by reflection in a plane of symmetry, the dissymmetric coupling constant situation results in observable nonequivalence. Thus, this compound is also of the AA'BB'XX' type.

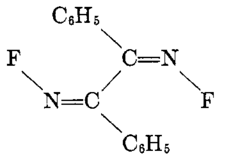
Solubility has limited study of the *meso* diastereoisomer. Acetone dissolves sufficient material to give strong spectra, but the chemical shifts are not sufficiently different to distinguish clearly the shifts of the nonequivalent F^{19} atoms. Similarly, the proton spectrum is insufficiently resolved to allow detailed interpretation.

Dehydrofluorination of Ia and Ib with triethylamine or other bases gave α,α'-bis(fluorimino)bibenzyl (II) as a mixture of *syn* and *anti* isomers. All of the three isomers of II shown were present according to the F^{19} nmr spectra. One isomer, a solid of mp 62°, was isolated in pure form; the F^{19} spectrum had a single peak at ϕ −35.5. The liquid isomer whose F^{19} nmr spectrum, doublets with J_{FF} = 20 cps at ϕ −28.4 and −36.6, indicated nonequivalent fluorine atoms

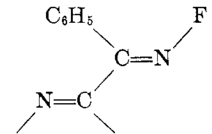


$$C_6H_5\underset{NF_2}{\overset{H}{C}}—\underset{NF_2}{\overset{H}{C}}C_6H_5 \xrightarrow{\text{base}} C_6H_5\overset{NF}{\overset{\|}{C}}—\overset{NF}{\overset{\|}{C}}C_6H_5$$

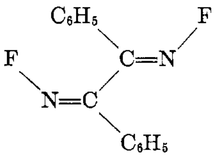
II



IIa



IIb



IIc

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(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Inc., New York, N. Y., 1965, p 888.

(8) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

was, of course, assigned the *syn-anti* structure (IIc). The remaining fluorine had an F^{19} peak at ϕ −36.0. In both IIa and IIc it appears that the aromatic ring would shield the fluorine atom to a considerable extent, and on the basis of the evidence on hand no further assignment of structure can be made.[9]

Experimental Section

Preparation of *meso*- and *dl*-α,α′-Bis(difluoramino)bibenzyl.[2]—The procedure was close to that used by Cerfontain.[1] Chlorobenzene was the solvent and the mixture was flushed with nitrogen prior to adding tetrafluorohydrazine from a pressurized cylinder. Thus, 10.0 g of *trans*-stilbene in 70 ml of chlorobenzene was stirred under 1 atm (600–800 mm) of tetrafluorohydrazine. The solution was warmed and stirred magnetically; at 75° a noticeable uptake of N_2F_4 occurred. The mixture was stirred 4 hr at 75°, but tetrafluorohydrazine uptake was complete in 3 hr. The chlorobenzene solution and an insoluble solid were washed from the reaction flask with methylene chloride. Methylene chloride was removed at reduced pressure, and the residual chlorobenzene solution was chilled in ice–water. Filtration gave 4.78 g of solid, mp 158–159°. The filtrate was reduced to dryness *in vacuo* and the residue was recrystallized from ligroin three times to give an additional 1.04 g of *meso*-α,α′-bis(difluoramino)-bibenzyl, mp 157–158°.

Anal. Calcd for $C_{14}H_{12}N_2F_4$: C, 59.15; H, 4.26; N, 9.86. Found: C, 59.60; H, 4.48; N, 9.88.

The combined ligroin filtrates were reduced in volume and chilled; 5.94 g of material, mp 107–110°, was obtained. When this material was again dissolved in ligroin, 0.06 g of material, mp 156–157°, remained. Two additional crops of *dl*-α,α′-bis-(difluoramino)bibenzyl were obtained from the filtrate of the 5.94-g crop; the first weighed 2.42 g, mp 111.5–113°, and the second weighed 0.57 g, mp 110–112°.

Anal. Calcd for $C_{14}H_{12}F_4$: C, 59.15; H, 4.26; N, 9.86. Found: C, 59.03; H, 4.63; N, 10.22.

Dehydrofluorination of the Stilbene–Tetrafluorohydrazine Adduct.—The adduct from 5 g of *trans*-stilbene and excess N_2F_4 was dissolved in 100 ml of methylene chloride. Then 8.3 ml (60 mmoles) of triethylamine in 25 ml of methylene chloride was added dropwise. After 3 hr at 35°, the mixture was washed with water, dilute aqueous hydrochloric acid, and water. Evaporation of the methylene chloride left 6.9 g of residue. This residue was chromatographed on silica gel; elution was carried out with pentane–methylene chloride (1:20 to 1:1). In fractions 8–23, 6.00 g of α,α′-bis(fluorimino)bibenzyl was eluted.

Anal. Calcd for $C_{14}H_{10}F_2N_2$: C, 68.84; H, 4.13; N, 11.47. Found (for fraction 9): C, 68.73; H, 4.34; N, 11.68. (F^{19} nmr spectrum showed singlet, ϕ −36.) Found (for fraction 13): C, 68.58; H, 4.11; N, 11.45. (F^{19} nmr spectrum showed doublets, ϕ −36.6, ϕ −28.4, J_{FF} = 20 cps.) Found (for fraction 19, a solid which was recrystallized from hexane, mp 62–63°): C, 68.38; H, 3.82; N, 11.36. (F^{19} nmr spectrum showed a single peak, ϕ −35.5.)

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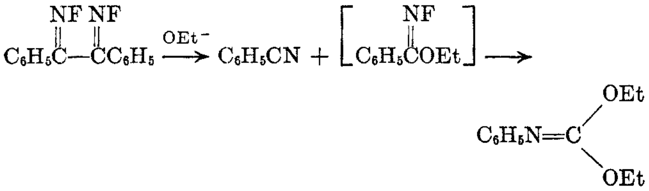
[9] Although the mixture of the fluorimines II was stable to alcohol, exposure to excess sodium ethoxide in ethanol produced benzonitrile and



$$C_6H_5\overset{NF}{\overset{\|}{C}}-\overset{NF}{\overset{\|}{C}}C_6H_5 \xrightarrow{OEt^-} C_6H_5CN + \left[C_6H_5\overset{NF}{\overset{\|}{C}}OEt\right] \longrightarrow C_6H_5N{=}C(OEt)_2$$

N-phenyl diethylimidocarbonate. This is an example of a Beckmann cleavage reaction under basic conditions.

The Electrolytic Reduction of Organomercuric Acetates in the Presence of Carbon Tetrachloride

Kunihisa Yosahida and Shigeru Tsutsumi

Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka, Japan

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The photolysis of organomercury compounds occurs by initial fission to form organomercury radical and organo radical. Diphenylmercury[1] reacts with carbon tetrachloride or chloroform to form phenylmercuric chloride, hexachloroethane, and chlorobenzene or benzene, respectively; the reactions are represented by the following scheme. Namely, the phenylmercury

$$\begin{gathered}
Ph_2Hg \xrightarrow{h\nu} PhHg\cdot + Ph\cdot \\
PhHg\cdot + CCl_3X \longrightarrow PhHgCl + \cdot CCl_2X \\
Ph\cdot + CCl_3X \longrightarrow PhX + \cdot CCl_3 \\
2\cdot CCl_3 \longrightarrow C_2Cl_6 \\
X = Cl \text{ or } H
\end{gathered}$$

radical abstracts the chlorine atom of the solvent. Phenylmercuric chloride is also formed by pyrolysis of diphenylmercury in the presence of carbon tetrachloride.[2] Moreover, dibenzylmercury[3] is photolyzed in chloroform to produce bibenzyl and mercurous chloride. On this occasion, it is not certain whether the benzylmercury radical abstracts the chlorine atom of the solvent to form intermediately benzylmercuric chloride.[4]

Besides, it is known that organomercury radicals disproportionate to diorganomercury compounds and mercury[5] or dissociate to organo radicals and mercury.[6]

With these in view, the electrolytic reduction of organomercuric acetates was conducted to investigate the behavior of organomercury radicals in the presence of carbon tetrachloride.

A solution of organomercuric acetate (0.01 mole) and carbon tetrachloride (30 ml) in methanol (60 ml) was electrolyzed. The results are summarized in the Table I.

TABLE I

REACTION PRODUCTS

RHgOAc		Products, g			Recovered
R	Wt, g	RHgCl	R_2Hg	Hg	RHgOAc, g
Ph	3.37	1.21	0.46	0.41	0.85
$PhCH_2$	3.51	0.05	0.87	0.50	1.02
C_6H_{11}	3.43	1.05	0.11	0.40	0.49

These are consistent with the following reactions (eq 1–4). It is not certain whether the reduction occurs directly (eq 1) or *via* the preionization followed by

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(1) G. A. Razuvaev and Yu. A. Ol'dekop, *Zh. Obshch. Khim.*, **19**, 736 (1949).

(2) G. A. Razuvaev and Yu. A. Ol'dekop, *ibid.*, **23**, 587 (1953).

(3) G. A. Razuvaev and Yu. A. Ol'dekop, *ibid.*, **19**, 1487 (1949).

(4) (a) It has been supposed that the benzylmercury radical abstracts the iodine atom from benzyl iodide.[4b] (b) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 39 (1963).

(5) (a) J. L. Maynard and H. C. Howard, Jr., *J. Chem. Soc.*, 960 (1923); (b) B. G. Gowenlock and J. Trotman, *ibid.*, 2114 (1957); (c) ref 4b; (d) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 460 (1966).

(6) (a) Reference 4b; (b) C. H. Wang, *J. Am. Chem. Soc.*, **85**, 2339 (1963); (c) G. N. O'Connor, J. V. Crawford, and C. H. Wang, *J. Org. Chem.*, **30**, 4090 (1965).