After additional extraction of impurities with benzene in a Soxhlet extraction apparatus and drying, the green solid was submitted for elemental analysis.

Anal. Calcd for $C_{20}H_{19}Ti_2Cl_4$: C, 48.34; H, 3.85; Ti, 19.28; Cl, 28.53. Found: C, 48.39, 48.43; H, 3.83, 3.84; Ti, 19.34, 19.35; Cl, 28.31, 28.33.

Reaction of Titanocene with *meso*-Stilbene Dichloride.—*meso*-Stilbene dichloride (0.50 g, 2.0 mmol) and 9 ml of benzene were added separately to a solution of titanocene (0.36 g, 2.0 mmol) in 5 ml of benzene with stirring. The reaction was exothermic with considerable foaming. After the reaction mixture had been stirred for 24 hr at room temperature, the contents were exposed to air and filtered. The green filter cake was washed with benzene and dried; it weighed 0.4 g (80%). The filtrate was evaporated to dryness and the residue was extracted with boiling petroleum ether. From the combined extracts three crystalline crops were collected, combined, and dried under vacuum. The dry, flaky crystals, which were identified as *trans*-stilbene, were recrystallized from petroleum ether. The final product weighed 0.23 g, mp 122–124° (lit.[6] mp 124°), corresponding to a yield of 64.0%.

Reaction of Titanocene with *trans*-Diiodostilbene.—Benzene (30 ml) was added to a solid mixture of titanocene (1.20 g, 6.74 mmol) and *trans*-diiodostilbene (1.45 g, 3.36 mmol). The mixture was stirred for 24 hr at room temperature. The contents were then filtered and the brownish-green filter cake was washed with benzene. The filtrate was evaporated to dryness and the residue was extracted with boiling pentane. The pentane extracts were combined and evaporated. The remaining residue was recrystallized from pentane and dried. The product, identified as diphenylacetylene, weighed 0.41 g, mp 60–61° (lit.[7] mp 64°), corresponding to a yield of 34.2% based on titanocene and 68.6% based on *trans*-diiodostilbene used in the reaction.

Registry No.—Titanocene, 1271-29-0.

[6] "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Co., Cleveland, Ohio, 1967, p C-546.

[7] Reference 6, p C-321.

Preparation of *N*,*N*-Bis(2-fluoro-2,2-dinitroethyl)amides

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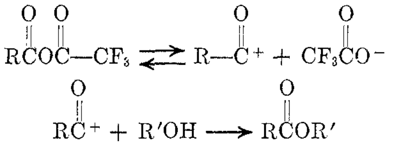
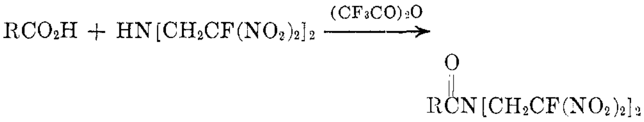
In a recent paper by Adolph and Kamlet[1] the preparation of bis(2-fluoro-2,2-dinitroethyl)amine (**1**) was reported. These authors showed that **1** was weakly basic; it could be recrystallized unchanged from trifluoroacetic acid, was insoluble in 50% sulfuric acid, and did not form isolable salts with mineral acids.[2] The weak nucleophilic properties of the amine **1** toward protons appear to parallel equally weak nucleophilic properties toward carbon. Attempts to prepare amides by the reaction of **1** with anhydrides or acyl chlorides or by ester amination, under usual conditions, proved fruitless.

Mixed trifluoroacetic–carboxylic anhydrides have been extensively used as mild reagents for preparing esters.[3] It has been postulated that the reactive species is the acylium ion, formed in equilibrium with the mixed anhydride.[4] In contrast, the main reaction course with amines involves a nucleophilic attack directly on the mixed anhydride, forming the trifluoroacetamide as the predominant product.[5] Thus, the method has been considered unsuitable for N-acylation.[3a] It seemed likely, however, that bis(fluorodinitroethyl)amine **1**, because of its lack of basic properties, would react *via* an acylium ion mechanism, if it reacted at all. Therefore an investigation of the reaction of mixed anhydrides with **1** was undertaken.



$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}{-}CF_3 \rightleftarrows R{-}\overset{O}{\overset{\|}{C}}{}^+ + CF_3\overset{O}{\overset{\|}{C}}O^-}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}{}^+ + R'OH \longrightarrow R\overset{O}{\overset{\|}{C}}OR'}$$



$$\mathrm{RCO_2H + HN[CH_2CF(NO_2)_2]_2 \xrightarrow{(CF_3CO)_2O} R\overset{O}{\overset{\|}{C}}N[CH_2CF(NO_2)_2]_2}$$

Bis(fluorodinitroethyl)amine **1** reacted at ambient temperature with the mixed anhydride formed by the addition of acetic acid to trifluoroacetic anhydride. The reaction, as judged by tlc analysis,[6] was complete and essentially quantitative in 24 hr. The reaction time for the mixed anhydride of butyric acid was 48 hr and for isobutyric acid 192 hr at ambient temperature. Pivalic acid was completely unreactive. That steric factors can play an important and even overriding role is not unexpected in view of the bulky nature of the amine.

With acrylic acid, a 69% yield of *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)acrylamide (**5**) was obtained after 4 days at ambient temperature. Fumaric and succinic acid did not react under these conditions, presumably because of the formation of the unreactive cyclic anhydrides.[3a] Ethyl fumarate, however, gave a 44% yield of ethyl *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)fumaramate (**6**) after 5 days at 80°. Chloroacetic acid required a longer reaction period of 25 days at 80°, while dichloroacetic acid was unreactive at 100° for periods up to 13 days. In contrast to dichloroacetic acid, a 71% yield of ethyl *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)oxamate was isolated from the reaction of the mixed anhydride of ethyl oxalate with **1** after 5 days at 100°.

For an acylium ion mechanism it would be expected that electronegative substituents on the carboxylic acid would inhibit the reaction by lowering the equilibrium concentration of both the mixed anhydride and the acylium ion. In general the experimental results are in accord with this expectation. However, an examination of the collected results in Table I indicates that ethyl oxalate reacts more readily than would be anticipated on the basis of inductive effects. The

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[1] H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, **34**, 45 (1969).

[2] A pK_a value of 0.4 can be calculated for **1** using Hall's correlation equation for secondary amines (ref 2a) and a σ^* value of 1.57 for the fluorodinitroethyl group (ref 2b). However, the data of Bagal and coworkers (ref 2c) indicates that amines substituted with bulky nitro groups are less basic than would be expected solely on the basis of inductive effects. A more reasonable figure for the pK_a of **1** would be ~ -0.3. (a) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **79**, 5441 (1951). (b) L. A. Kaplan and H. B. Pickard, *J. Org. Chem.*, **35**, 2004 (1970). (c) L. I. Bagal, G. I. Koldobskii, and E. S. Gerasimova, *Zh. Org. Khim.*, **3**, 2084 (1967).

[3] (a) J. M. Tedder, *Chem. Rev.*, **55**, 787 (1955); (b) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965); L. Alimirante and G. Tosolini, *ibid.*, **26**, 177 (1961).

[4] For a comprehensive discussion of the possible equilibria involved in mixed anhydrides see ref 3a.

[5] E. J. Bourne, S. H. Henry, C. E. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952).

[6] W. H. Gilligan, *J. Org. Chem.*, **36**, 2138 (1971).

TABLE I

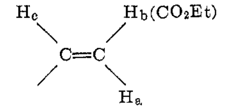
PREPARATION OF N,N-BIS(2-FLUORO-2,2-DINITROETHYL)CARBOXAMIDES $RC(=O)N[CH_2CF(NO_2)_2]_2$

			Reaction conditions					Anal.,[b] %			
Compd	RCO_2H, R =	σ_R^{*a}	Molar ratio of reactants Amine 1: Acid:TFAA	Temp, °C	Time, days	Yield, %	Mp, °C	C	H	F	N
2	CH_3	0.0	1:2.5:4.0	Ambient	1	82	77–78	21.76	2.13	11.48	21.15
								21.96	2.11	11.63	21.05
3	$CH_3CH_2CH_2$	−0.12	1:2.5:4.0	Ambient	2	98	55–56	26.75	3.09	10.58	19.50
								26.69	3.01	10.44	19.36
4	$(CH_3)_2CH$	−0.13	1:2.5:4.0	Ambient	8	92	64–65	26.75	3.09	10.58	19.50
								26.61	2.99	10.52	19.60
	$(CH_3)_3C$	−0.30	1:2.5:4.0	Ambient	>30						
5	$H_2C{=}CH$	0.36	1:6.1:6.1	Ambient	4	69	111–113	24.50	2.06	11.07	20.41
								24.45	2.08	11.22	20.06
6	$EtO_2CCH{:}CH$	0.62	1:4.3:4.3	80	5	44	85–86	28.92	2.67	9.15	16.87
								28.83	2.73	9.02	16.62
7	$ClCH_2$	1.05	1:4.0:4.0	80	25	42	87–88	19.71	1.66	10.39	19.16
								19.60	1.43	10.16	18.84
8	EtO_2C	2.00	1:4.3:4.3	80	5	41	73–74	24.69	2.33	9.76	18.00
			1:4.3:4.3	100	5	71		24.55	2.18	9.58	18.04
	Cl_2CH	1.94	1:4.3:4.3	100	13						

[a] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13. [b] Upper line, calculated value; lower line, experimental value.

TABLE II

INFRARED AND PMR ABSORPTION BANDS OF N,N-BIS(2-FLUORO-2,2-DINITROETHYL)CARBOXAMIDES

		Ir, cm^{-1}		Pmr, δ^a				
Compd	$RCON[CH_2CF(NO_2)_2]_2$, R =	CO (amide 1)	CO (ester)	$FCCH_2$	CH_3	CH_2		Miscellaneous
2	CH_3	1703		4.80 (d)	2.22 (s)			
3	$CH_3CH_2CH_2$	1697		4.80 (d)	0.95 (t)	1.66 (m) 2.34 (t)		
4	$(CH_3)_2CH$	1691		4.80 (d)	1.15 (d)			2.75 (m, CH)
5	$H_2C{=}CH$	1685		5.15 (d)			6.76 (m, H_c) 6.46 (d), 6.29 (d, H_a) 5.98 (d), 5.88 (d, H_b)	
6	$EtO_2CCH{=}CH$	1687	1728	4.89 (d)	1.30 (t)	4.24 (q)	7.17 (d, H_c) 6.85 (d, H_a)	
7	$ClCH_2$	1705		4.90 (d)		4.33 (s)		
8	EtO_2C	1708	1744	5.01 (q)	1.42 (t)	4.41 (q)		

[a] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

reason for this apparent discrepancy is not obvious and further investigation appears warranted.

Collected in Table II are the ir and pmr absorption bands for the carboxamides **2–8**. The CO (amide 1) band for N,N-bis(fluorodinitroethyl)acrylamide **5** is at 1685 cm^{-1} and for ethyl N,N-bis(fluorodinitroethyl)-fumaramate **6** at 1687 cm^{-1}, indicating that there may be a small shift of about 10 cm^{-1} to lower frequencies owing to conjugation. This effect is more apparent for the CO (ester) band of **6**. For the other compounds, the CO (amide 1) band falls in the range 1691–1708 cm^{-1}. The NO_2 asymmetric stretching vibration (1604–1613 cm^{-1}),[7] the NO_2 symmetric stretching vibration (1310–1315 cm^{-1}),[7] and the C–N modes (849–852 and 805–807 cm^{-1})[7] were within the ranges expected for fluorodinitroethyl compounds.[8] The *trans*-CH=CH out-of-plane deformation vibration appeared at 974 cm^{-1} for **6**.

The pmr spectra showed a broadened doublet ($FCCH_2$, J_{HF} = 13 ± 0.5 Hz) at 4.80–5.15 ppm for compounds **2–7**. Ethyl N,N-bis(2-fluoro-2,2-dinitroethyl)-oxamate (**8**) exhibited a broadened quartet at 5.01 ppm (J_{HF} = 13 Hz). The olefinic protons of the acrylamide **5** showed a typical ABX pattern ($J_{H_aH_c} = 17$, $J_{H_bH_c} = 10$, $J_{H_aH_b} = 2$ Hz) and of the fumaramate **6** a simple *trans*-HH pattern (J_{HH} = 15 Hz). For the latter compound there was no indication of any band that could be correlated with the *cis*-CH=CH structural moiety. Other absorption bands associated with CH_2 and CH_3 groups are unexceptional with J_{HH} values of 7 ± 0.5 Hz. Area ratios corresponded to the assigned structures.

There are a large number of both aliphatic and aromatic amines of low basicity. It would seem, based on these results, that many would be suitable compounds for N-acylation by mixed anhydrides, contrary to statements in the literature.

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(7) Not shown in Table II.

(8) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

Experimental Section

General (Caution).—The polynitro compounds described in this paper are explosives and should be handled with due care. In particular, reactions, should be run on a small scale (1 or 2 g) behind adequate shielding with careful attention to temperature control. Handling of hot reaction vessels should be strictly avoided. Personnel should be equipped with full face masks, heavy rubber gloves, and fire-retardant laboratory coats.

Pmr spectra were obtained in deuteriochloroform solution with tetramethylsilane as the internal standard using a Varian HA-100 spectrometer. Infrared spectra were obtained in 1,2-dichloroethane solution using a Beckman IR-4 spectrometer. Melting points are uncorrected.

General Directions for Preparing *N,N*-Bis(2-fluoro-2,2-dinitroethyl)amides.—The reactants in the proportions given in Table I were combined in a stoppered flask and stirred magnetically until the amine **1** was dissolved. The flask was then allowed to stand at ambient temperature for the indicated time, while samples were withdrawn periodically to monitor the course of the reaction by tlc. For reactions run at higher temperatures the flask was equipped with a reflux condenser topped with a drying tube filled with calcium sulfate.

After the indicated time had elapsed, the crude mixture was taken up in methylene chloride and washed consecutively with water, 0.4 *N* NaOH, and water. After drying with magnesium sulfate and filtering, volatiles were removed *in vacuo*. If crystallization did not occur spontaneously, the crude product was purified by column chromatography on silica gel (G. Frederick Smith Co., 50–200 mesh). Benzene was used as the eluent. Recrystallization was from methylene chloride or methylene chloride–carbon tetrachloride mixtures.

Registry No.—**2**, 35666-43-4; **3**, 35666-44-5; **4**, 35666-45-6; **5**, 35666-46-7; **6**, 35666-47-8; **7**, 35666-48-9; **8**, 35666-49-0.

The Synthesis of *cis*- and *trans*-1-Methyl-2,5-diphenylpyrrolidines by the Leuckart Reaction of 1-Benzoyl-2-phenylcyclopropane[1]

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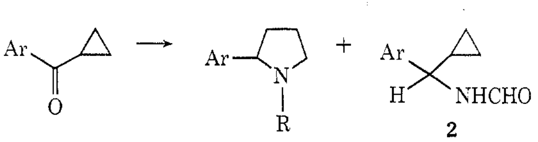
Received March 8, 1972

Previously we reported that the Leuckart reaction of cyclopropyl aryl ketones with formamide gives predominantly the rearranged products 1-formyl-2-arylpyrrolidines (**1a**), in addition to small amounts of the normal products (**2**).[2] Subsequently we observed that the reaction of *N*-methylformamide with cyclopropyl phenyl ketone, which proceeds considerably more slowly than that of the formamide, occurs with exclusive rearrangement, giving in high yield 1-methyl-2-phenylpyrrolidine (**1b**, Ar = Ph).[3] Using this reaction we achieved a one-step synthesis of nicotine (**1b**, Ar = 3-pyridyl) from cyclopropyl 3-pyridyl ketone.[3]



1a, R = CHO
b, R = CH_3

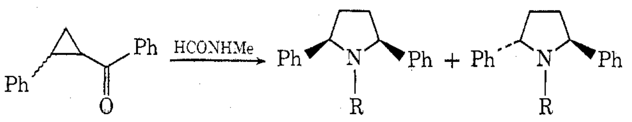
2

In this paper we wish to describe results obtained from the Leuckart reaction of 1-benzoyl-2-phenylcyclopropane with *N*-methylformamide. This work was undertaken to study the direction of the cyclopropane ring opening and the stereochemistry of the reaction.

Results

A mixture of *cis*- and *trans*-1-benzoyl-2-phenylcyclopropane (**3**) was obtained from the reaction of benzalacetophenone and dimethylsulfoxonium methylide.[4] This mixture of stereoisomeric ketones was heated to 180° with *N*-methylformamide in the presence of catalytic amounts of magnesium chloride for 25 hr. After this period of time gas chromatographic analysis indicated the absence of ketone and the presence of two products in the ratio of 2:1, in a total yield of 50%.

The products were separated by chromatography on silica gel. The major component was identified as *cis*-1-methyl-2,5-diphenylpyrrolidine (**4b**), while the minor component was found to be the trans isomer (**5b**).



3

4a, R = H
b, R = Me

5a, R = H
b, R = Me

These structure assignments were confirmed by independent syntheses. Thus we have prepared *cis*- and *trans*-2,5-diphenylpyrrolidine[5] (**4a** and **5a**, respectively), which were converted to the respective *N*-methyl derivatives (**4b** and **5b**) by formic acid–formaldehyde. The *cis*- and *trans*-1-methyl-2,5-diphenylpyrrolidines so obtained were found identical in every respect with the products obtained in our reaction. Nmr data are given in Table I.

In order to study the possible influence of the stereochemistry of starting material, we have prepared pure *cis*-1-benzoyl-2-phenylcyclopropane.[6] Reaction of this ketone with *N*-methylformamide yielded a mixture of **4b** and **5b** in the same yield and ratio as those obtained in the previous reaction.

The absence of 2,4-diphenylpyrrolidines was confirmed by comparison of the product mixture with samples prepared by a known reaction.[7]

The formation of products **4b** and **5b** can be rationalized by assuming that attack of *N*-methylformamide upon the carbonyl group of **3** produces a hydroxyformamide type intermediate[8] which dissociates to an

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[1] A preliminary account of this study was presented at the 39th Meeting of the Israel Chemical Society, Jerusalem, Sept 29–Oct 1, 1969. E. Breuer and D. Melumad, *Israel J. Chem.*, **7**, 31 (1969).

[2] E. Breuer and Y. Stein, *ibid.*, **6**, 901 (1968).

[3] E. Breuer and D. Melumad, *Tetrahedron Lett.*, 3595 (1969).

[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[5] C. G. Overberger, M. Valentine, and J. P. Anselme, *ibid.*, **91**, 687 (1969).

[6] H. M. Walborsky and L. Plonsker, *ibid.*, **83**, 2138 (1961).

[7] M. C. Kloetzel, *ibid.*, **69**, 2271 (1947).

[8] M. L. Moore, *Org. React.*, **5**, 301 (1949).