TABLE I

NMR DATA OF *cis*- AND *trans*-2,5-DIPHENYLPYRROLIDINES AND THEIR *N*-METHYL DERIVATIVES[a]

Compd	Aromatic (10 H)	Benzylic (2 H)	*N*-Methyl (3 H)
4a	7.27	4.25	
5a	7.23	4.43	
4b	7.31	3.34	1.98
5b	7.22	4.10	1.88

[a] Given in δ values; $CDCl_3$ solution with TMS as internal standard.

immonium–carbonium ion that is capable of rearranging to a pyrroline derivative.[9,10] The latter is reduced *in situ* by formic acid to products **4b** and **5b**.[11] The predominant formation of the cis product **4b** is in agreement with what is known concerning the stereochemistry of the Leuckart reaction.[12]

Experimental Section[13]

1-Benzoyl-2-phenylcyclopropane (**3**) (a mixture of isomers) was prepared by the action of dimethylsulfoxonium methylide on benzalacetophenone,[4] mp 45–50° (lit.[4] mp 45.5–50.0°). The spectral properties of the material were in agreement with those published.[4]

***cis*-1-Benzoyl-2-phenylcyclopropane** was prepared by the action of phenyllithium on *cis*-2-phenylcyclopropanecarboxylic acid, mp 68–70° (lit.[6] mp 69–70°).

Reaction of *N*-Methylformamide with 1-Benzoyl-2-phenylcyclopropane.—A mixture of 5.5 g (0.025 mol) of ketone, 9 g of *N*-methylformamide, and 0.32 g (0.0025 mol) of $MgCl_2 \cdot 2H_2O$ was heated in an oil bath at 180° for 24 hr under N_2. The reaction mixture was dissolved in dilute hydrochloric acid and extracted several times with ether. The aqueous acidic solution was made alkaline by the addition of sodium hydroxide, and extracted five times with ether. After drying, the ether was evaporated to give a residue (2.5 g). This mixture was separated by chromatography on silica gel. Elution with benzene gave pure *cis*-1-methyl-2,5-diphenylpyrrolidine (**4b**), mp 60° (1.6 g). The compound was further purified by collecting a sample by preparative gas chromatography.

Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.47; H, 8.04; N, 5.75.

The picrate had mp 152° from ethanol.

Anal. Calcd for $C_{23}H_{22}N_4O_7$: C, 59.22; H, 4.75; N, 12.01. Found: C, 59.45; H, 4.94; N, 12.29.

Further elution with benzene–chloroform (1:1) provided pure *trans*-1-methyl-2,5-diphenylpyrrolidine (**5b**) as a colorless oil (0.8 g). Purification by preparative gas chromatography gave an analytical sample.

Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.05; H, 7.86; N, 6.04.

The picrate had mp 175° from ethanol.

Anal. Calcd for $C_{23}H_{22}N_4O_7$: C, 59.22; H, 4.75; N, 12.01. Found: C, 59.35; H, 5.04; N, 12.08.

2,4-Diphenylpyrrolidine was prepared according to Kloetzel by hydrogenation of 4-nitro-1,3-diphenyl-1-butanone,[7] bp 165° (1.5 mm) [lit.[7] bp 182.5° (3.8 mm)]. The product gave a benzamide, mp 122° (lit.[7] mp 122–124°).

Methylation of 2,4-diphenylpyrrolidine was carried out according to Icke, *et al.*,[14] using 1.56 g of 2,4-diphenylpyrrolidine, 1.75 ml of formic acid, and 1.60 ml of a 30% solution of formaldehyde. After work-up 1.0 g of product was isolated by distillation, bp 120° (0.5 mm).

Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.25; H, 8.23; N, 5.88.

The nmr spectrum of the product showed the aromatic protons at δ 7.5–7.1 (m, 10 H), the N–Me protons as two singlets in the ratio of approximately 1:3 at 2.25 and 2.18, respectively, and the rest of the protons as multiplets at 3.7–1.6.

Registry No.—*cis*-**3**, 1145-91-1; *trans*-**3**, 1145-92-2; **4a**, 22147-83-7; **4b**, 35657-63-7; **4b** picrate, 35657-64-8; **5a**, 22147-84-8; **5b**, 35657-66-0; **5b** picrate, 35657-67-1; 1-methyl-2,4-diphenylpyrrolidine, 35657-68-2.

(9) J. B. Cloke, *J. Amer. Chem. Soc.*, **51**, 1174 (1929).

(10) Rearrangement of the cyclopropyl ketimine to a pyrroline by a concerted mechanism does not seem likely, as no 2,4-diphenylpyrrolidines were found in the product mixture.

(11) For similar reductions of enamines see N. J. Leonard and R. R. Sauers, *J. Amer. Chem. Soc.*, **79**, 6210 (1957).

(12) In all known examples of this reaction the product resulting from the approach of the reducing agent from the least hindered side predominates: (a) D. G. Hey, G. D. Meakins, and T. L. Whateley, *J. Chem. Soc. C*, 1509 (1967); (b) M. Davis, E. W. Parnell, and D. Warburton, *ibid.*, 1688 (1966); (c) D. S. Noyce and F. W. Bachelor, *J. Amer. Chem. Soc.*, **74**, 4577 (1952); (d) P. F. Coe, B. C. Uff, and J. W. Lewis, *J. Chem. Soc. C*, 2265 (1968); (e) R. R. Sauers, *J. Amer. Chem. Soc.*, **80**, 4721 (1958).

(13) All boiling points and melting points are uncorrected. Nmr spectra were measured by a Jeol C-60H instrument in $CDCl_3$; all chemical shifts are given in parts per million downfield from TMS. All gas chromatographic work was carried out on an F & M Model 720 dual column programmed temperature gas chromatograph on a 6 ft × 0.25 in., 10% diethylene glycol succinate on Chromosorb W column. Microanalyses were carried out by the Hebrew University Microanalytical Laboratory.

(14) R. N. Icke, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 723.

Structure and Proton Magnetic Resonance Study of 3-(*N'*-Aziridinyl)succinimides[1a]

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In an earlier communication,[2] it was shown that reaction of N-substituted maleimides with ethereal solutions of diazomethane gave instantaneously the corresponding pyrazolines in high yields. Extending further the studies on the reactivity of maleimides, we describe now the results obtained with aziridine.[3]

Mild treatment of N-substituted maleimides with aziridine gave solid adducts whose elemental composition corresponded to the combination of equimolecular amounts of aziridine and of the maleimide.

The adducts showed an infrared absorption band at 1720 cm^{-1} corresponding to the imide carbonyl groups. Their 100-MHz pmr spectra showed, in addition to the signals of the N substituent, the presence of an ABX system (δ_A 3.01, δ_B 2.90, and δ_X 2.59 ppm; J_{AB} = 18, J_{AX} = 7.5, and J_{BX} = 4.5 Hz) attributable to a $-CH_2-CH-$ moiety on a five membered ring. The CH signal is found at higher fields than the AB signals of the methylene group. In the high field region there is a strongly coupled four-proton system, which even at 220 MHz remained complex. It showed signals at 2.036 (1 H), ~1.873 (2 H), and 1.359 (1 H) ppm. In view of these results, and considering that N-substituted

(1) (a) Presented at the VII Congreso Mexicano de Química Pura y Aplicada, Morelia, Mich., México, April 1972. (b) This work is part of the M.S. thesis of E. G. G. who receives a CoNaCyT (México) scholarship (1970–1972).

(2) V. Mendoza, P. Joseph-Nathan, and C. Perez, *Rev. Soc. Quim. Mex.*, **15**, 103 (1971).

(3) O. C. Dermer and G. E. Man, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, Chapter 3.

aziridines provide relatively simple pmr spectra,[4-8] some chemical reactions were done to establish the structure of the adducts.

Treatment of the adduct (IIb), derived from *N*-(*p*-methoxyphenyl)maleimide (Ib), with sodium borohydride gave *N*-(*p*-methoxyphenyl)succinimide which was identified by direct comparison with an authentic sample.[9] Catalytic hydrogenation of IIb gave a compound to which structure IIIa could be ascribed. Its 100-MHz-pmr spectrum showed, in addition to the *p*-methoxyphenyl moiety, and ABX system (δ_A 2.65, δ_B 3.00, and δ_X 3.88 ppm; J_{AB} = 18; J_{AX} = 6, and J_{BX} = 8 Hz) corresponding to the five-membered ring protons, a NH signal at 1.85 ppm which disappeared after equilibration with D_2O and an ethyl group [triplet J = 7 Hz at 1.16 (3 H) ppm and quartet J = 7 Hz at 2.75 (2 H) ppm]. The acetyl derivative (IIIb) showed the absence of the NH signal and the presence of a new singlet (3 H) at 2.15 ppm.

Treatment of the original adduct (IIb) with acetic anhydride gave a compound $C_{17}H_{20}O_6N_2$, which showed ir bands at 1745 (ester carbonyl), 1720 (imide carbonyls), and 1650 cm^{-1} (amide carbonyl). The pmr spectrum is consistent with structure IV (see the Experimental Section).

The above chemical evidence confirms structure IIb. In order to explain the pmr signals, measurements in DMSO-d_6 were performed. Most signals still appear as when measured in $CDCl_3$ but the ABX system of the five-membered-ring protons showed now an AB_2 system at 3.05 and at 2.80 ppm in which the CH proton is found at lower fields than the methylene signals. Variable temperature measurements (see Figure 1) revealed that near 120° the signals of the high field, strongly coupled, four-proton aziridine system collapsed to a singlet (4 H) at 1.67 ppm. When the sample is cooled down again to room temperature the complex nmr pattern due to the protons of the aziridine ring reappeared. This indicates that at higher temperatures the aziridine ring rotates freely, that its nitrogen lone pair inverts fast in the nmr time scale, or that both phenomena are present since otherwise the protons of the ring would originate A_4 or A_2B_2 systems.[5,7] At room temperature there should therefore exist a preferred conformation of the three-membered ring in respect to the imide ring. In addition there is no evidence for slow invertion of the lone pair of the aziridine nitrogen which should cause duplicities of the CH signal bearing the three-membered ring.[10] This is not observed even at 220 MHz.

This suggests that an interaction of the lone pair of electrons of the aziridine nitrogen atom with the phenyl ring or with one of the carbonyl groups could exist. In order to obtain more information of this interaction, the adduct of aziridine and *N*-methylmaleimide (Ia) was prepared. The product (IIa) showed again the complex spin–spin pattern in the high field region of the pmr spectrum suggesting that the interaction is due to a carbonyl group and that there is restricted rotation around the C–N band.[10] An alternate less probable explanation could involve the two nitrogen atoms of the molecule. Unfortunately this could not be excluded since reaction of maleic anhydride and aziridine gave only polymeric material. Treatment

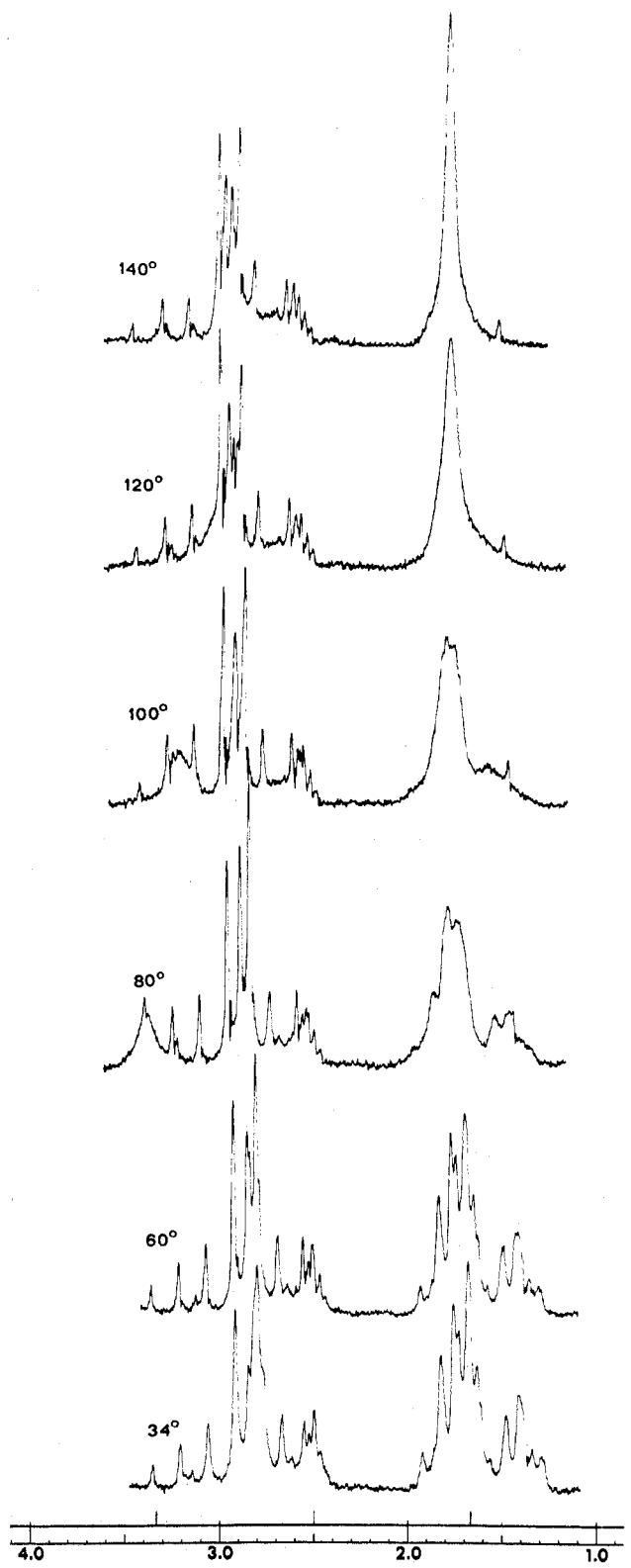
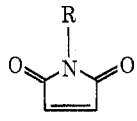


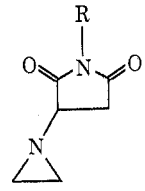
Figure 1.—High field region of the 60-MHz pmr spectra of *N*-(*p*-methoxyphenyl)-3-(*N'*-aziridinyl)succinimide (IIb) in DMSO-d_6 at various temperatures.

(4) M. Jautelat and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 642 (1969).
(5) S. J. Brois, *Tetrahedron*, **26**, 227 (1970).
(6) J. D. Andose, J.-M. Lehn, K. Mislow, and J. Wagner, *J. Amer. Chem. Soc.*, **92**, 4050 (1970).
(7) J. T. Rudesill, R. F. Severson, and G. Pomonis, *J. Org. Chem.*, **36**, 3071 (1971).
(8) D. L. Nogel, P. B. Woller, and N. H. Cromwell, *ibid.*, **36**, 3911 (1971).
(9) A. Arcosia, H. Lumbroso, and R. Passerini, *Bull. Soc. Chim. Fr.*, 754 (1959).
(10) D. J. Anderson, D. C. Horwell, and R. S. Atkinson, *J. Chem. Soc. C*, 624 (1971).

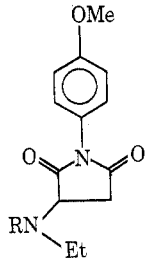
of *N*-(*p*-carbomethoxyphenyl)maleimide (Ic) with aziridine gave the corresponding adduct (IIc) whose pmr spectrum showed the complex high field signals.



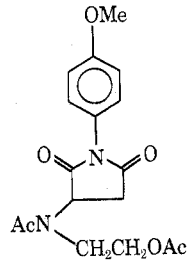
Ia, R = Me
b, R = *p*-MeOC$_6$H$_4$
c, R = *p*-MeOOCC$_6$H$_4$



IIa, R = Me
b, R = *p*-MeOC$_6$H$_4$
c, R = *p*-MeOOCC$_6$H$_4$



IIIa, R = H
b, R = Ac



IV

Experimental Section

Melting points are uncorrected. Infrared spectra were determined in $CHCl_3$ solutions on a Perkin-Elmer 421 spectrophotometer. Ultraviolet spectra were measured in 95% EtOH solutions using a Unicam SP-800 spectrophotometer. Nuclear magnetic resonance spectra were determined using Varian Associates A-60, HA-100, and HR-220 spectrometers. Variable temperature measurements were performed with the aid of V-6040 variable temperature controllers. Chemical shifts are in ppm relative to internal TMS. The elemental analysis were performed by the Alfred Bernhardt Laboratories, West Germany.

N-(*p*-**Methoxyphenyl**)-**3**-(*N'*-**aziridinyl**)**succinimide** (**IIb**).—A solution of 9 g of *N*-(*p*-methoxyphenyl)maleimide (**Ib**) in 250 ml of anhydrous ether and a few drops of pyridine was cooled in an ice bath and treated dropwise under stirring with aziridine, until the yellow solution was completely colorless. A small amount of a pale pink solid that is formed during the reaction was removed by filtration. The solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated. Crystallization from ether–hexane gave 7.5 g (69%) of white prisms, mp 103–104°. The analytical sample showed mp 105–106°; λ_{max} 218, 240, 271 mμ (ε 3000, 7700, 1500); ir bands at 1720 (carbonyl groups) and 1610 and 1590 cm^{-1} (C=C double bonds).

Anal. Calcd for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; O, 19.49; N, 11.38. Found: C, 63.56; H, 5.83; O, 19.54; N, 11.25.

N-**Methyl-3**-(*N'*-**aziridinyl**)**succinimide** (**IIa**).—Treatment of 1 g of *N*-methylmaleimide (Ia) as in the previous case gave 745 mg (54%) of IIa as prisms: mp 60–61°; λ_{max} 215, 248, 272 mμ (ε 800, 2200, 500); ir band at 1710 cm^{-1} (carbonyl groups).

Anal. Calcd for $C_7H_{10}O_2N_2$: C, 54.54; H, 6.54; O, 20.76; N, 18.17%. Found: C, 54.58; H, 6.63; O, 20.82; N, 18.04%.

N-(*p*-**Carbomethoxyphenyl**)-**3**-(*N'*-**aziridinyl**)**succinimide** (**IIc**).—Treatment of 5 g of Ic as in the previous cases gave 4 g (67%) of IIc as prisms: mp 113–114°; λ_{max} 218, 246 mμ (ε 2900, 11,200); ir bands at 1725 (carbonyl groups) and 1605 cm^{-1} (C=C double bonds); Rast 284, mol wt 274.

Anal. Calcd for $C_{14}H_{14}O_4N_2$: C, 61.31; H, 5.14; O, 23.33; N, 10.21. Found: C, 61.18; H, 5.25; O, 23.35; N, 10.08.

N-(*p*-**Methoxyphenyl**)**succinimide**.—A solution of 300 mg of IIb in 30 ml of tetrahydrofuran was refluxed during 5 hr in the presence of 300 mg of sodium borohydride. The mixture was cooled and filtered and the clear filtrate evaporated to a small volume. Upon addition of hexane, there crystallized 150 mg (60%) of *N*-(*p*-methoxyphenyl)succinimide, mp 151–153°. The analytical sample was obtained as white needles, mp 165–166°. This material was identified by standard procedures with a sample obtained by catalytic hydrogenation of *N*-(*p*-methoxyphenyl)maleimide.[8]

Catalytic Hydrogenation of IIb.—A solution of 500 mg of the compound in 80 ml of ethyl acetate was hydrogenated in the presence of 40 mg of prehydrogenated 10% Pd/C catalyst until the uptake of hydrogen ceased. The catalyst was removed by filtration and the solution concentrated to a small volume. Crystallization from ethyl acetate–hexane gave 432 mg (86%) of IIIa as white prisms mp 112–114°. The analytical sample (ether–hexane) showed mp 115–116°; λ_{max} 218, 237, 272 mμ (ε 4600, 9900, 2100); ir bands at 3310 (amine), 1710 (carbonyl groups), and 1610 and 1590 cm^{-1} (C=C double bonds).

Anal. Calcd for $C_{13}H_{16}O_3N_2$: C, 62.89; H, 6.50; O, 19.33; N, 11.28. Found: C, 62.98; H, 6.46; O, 19.39; N, 11.18.

Acetylation of IIIa.—Treatment of 300 mg of IIIa with Ac_2O–AcONa at room temperature during 12 hr, followed by work-up as usual, gave 197 mg (56%) of IIIb as white prisms: mp 117–118°; λ_{max} 218, 245, 272 mμ (ε 2900, 8700, 2600); ir bands at 1720 (imide carbonyls), 1640 (amide carbonyl), and 1610 cm^{-1} (C=C double bands).

Anal. Calcd for $C_{15}H_{18}O_4N_2$: C, 62.06; H, 6.25; O, 22.04; N, 9.65. Found: C, 62.17; H, 6.21; O, 22.23; N, 9.64.

Treatment of IIb with Acetic Anhydride.—A sample of 500 mg of IIb was treated with Ac_2O–AcONa as described above. Crystallization from ether–hexane gave 335 mg (47%) of IV as white prisms: mp 136–137°; λ_{max} 218, 236, 272 mμ (ε 4700, 8900, 1600); ir bands at 1745 (ester carbonyl), 1720 (imide carbonyls), 1650 (amide carbonyl), and 1610 and 1590 cm^{-1} (C=C double bonds); nmr methoxyl at 3.82 (s), acetyls at 2.15 (s) and 2.08 (s), aromatics at 7.20 (2 H) and 7.01 (2 H), NCH_2CH_2O at 4.22 (2 H) and 3.75 (2 H), and ring protons at 4.07 (1 H) and 3.00 (2 H) ppm.

Anal. Calcd for $C_{17}H_{20}O_6N_2$: C, 58.61; H, 5.79; O, 27.56; N, 8.04. Found: C, 58.56; H, 5.92; O, 27.48; N, 8.12.

Registry No.—IIa, 35740-37-5; IIb, 35740-75-1; IIc, 35740-76-2; IIIa, 35740-77-3; IIIb, 35740-78-4; IV, 35740-79-5.

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The Mechanism of Formation of Benzo[*g*]quinolones *via* the Combes Reaction

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Treatment of the condensation products of 2-aminonapthalene and 1,3-dicarbonyl compounds with H_2SO_4 provides a convenient method of synthesis of benzo[*g*]quinolines.[1-3] The formation of benzo[*g*]quinolines rather than the expected benzo[*f*]quinolines has been explained in two ways: Johnson[2] has proposed that the anil **1** affords linear products because of a larger deactivation of the one position with respect to the three position in the naphthalene ring; Huigsen[3]

(1) W. S. Johnson and F. J. Mathews, *J. Amer. Chem. Soc.*, **66**, 210 (1944).
(2) W. S. Johnson, E. Woroch, and F. J. Mathews, *ibid.*, **69**, 566 (1947).
(3) R. Huisgen, *Justus Liebigs Ann. Chem.*, **564**, 16 (1949).