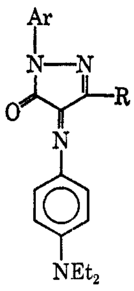
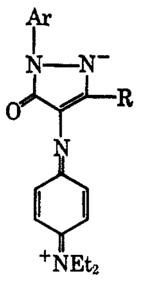


Va



Vb

In terms of the present dyes, this indicates that the pyrazolinyl-N bond order is higher than that of the adjacent phenyl-N bond. Loss of coplanarity of the pyrazolone and phenyl rings, occasioned by overcrowding, might well be expected to occur by the twisting of the weaker of these bridge bonds, *i.e.*, the phenyl-N bond. Such twisting would, however, lower its bond order even more thus increasing the energetic asymmetry of the dye, and cause a shift to shorter wavelengths.

If, however, the overcrowding results in the twisting of the pyrazolinyl-N bond, a point can be reached at which the bond orders of both bridge bonds are identical or nearly so. A result of this would be an increase in the polarity of the dye chromophoric system and an approach to an isoenergetic resonance system. In this case introduction of the crowding substituent would cause a shift to longer wavelengths accompanied by a decrease in the intensity of the absorption resulting from a reduction in π electron overlap. Support for this proposition is provided by the fact that the molecular extinction coefficient falls from[5] about 36,000 to 12,000 (for IV in ethyl acetate) on introduction of the second methyl group.

The x band for the crowded dye (IV) is, however, at a longer wavelength (640 nm) than that expected for an isoenergetic resonance system of the structure. This can be calculated[6] as the mean of the peaks of the related symmetrical dyes of which the present dyes are hybrids, *i.e.*, 578 nm, the mean of the pyrazolone oxonol anion (437 nm) and the Bindschedler's Green analog (725 nm).

It is known however that in isoenergetic dyes, *e.g.*, symmetrical cyanines, any loss of coplanarity of the end nuclei caused by steric hindrance will result in a shift to longer wavelength accompanied by a decrease in intensity, the magnitude depending on the degree of twisting.[7-9] This same effect may be operative in the present case.[10]

Experimental Section

Dyes I-III were prepared as described elsewhere.[3] Dye IV was prepared, by the same procedure, from 1-phenyl-3-methylpyrazolone and 4-amino-3,5-dimethyl-N,N-diethylaniline. It was purified by recrystallization from ethanol.

Anal. Calcd for $C_{22}H_{26}N_4O$: C, 72.9; H, 7.18; N, 15.5. Found: C, 72.9; H, 7.47; N, 15.2.

Visible absorption spectra were measured on a Unicam SP800 spectrophotometer and nmr spectra were measured on a Varian HA-100 spectrometer.

Registry No.—I, 4595-01-1; II, 4719-41-9; III (*syn*), 14071-78-4; III (*anti*), 14071-79-5; IV, 4719-38-4.

Acknowledgment.—We thank Dr. P. W. Vittum of the Eastman Kodak Co. for supplying a generous sample of 4-amino-3,5-dimethyl-N,N-diethylaniline.

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The Reaction of Azirines with Diazomethane to Produce Allylic Azides[1]

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As an extension of work carried out in this laboratory on the reactions of azirines,[2,3] it was considered of interest to determine the course of a cycloaddition reaction between diazomethane and representative azirines. 1,3-Dipolar cycloadditions of diazoalkanes to π bonds are well documented.[4,5] In particular, reaction of diazomethane with the C=C bond furnishes pyrazolines[6,7] and with the C=N bond, triazolines.[8] The related cycloaddition of azides to olefins gives triazoline adducts of varying stability.[9-14] Reported here is the reaction of diazomethane with the C=N in a three-membered ring,[15] the azirine system. The choice of the monomethyl azirine **1**, 3-methyl-2-phenyl-1-azirine, was dictated in part by the sluggish nature of the reaction with the dimethyl azirine **6**, 3,3-dimethyl-2-phenyl-1-azirine, and in part because the single substituent in the 3 position provided a marker for the ring carbon ($CHCH_3$) *vs.* the diazomethane carbon (CH_2) in following product formation.

When a chilled solution of diazomethane was added to a cold solution of 3-methyl-2-phenyl-1-azirine (**1**), both in ether, and the resulting solution was allowed to

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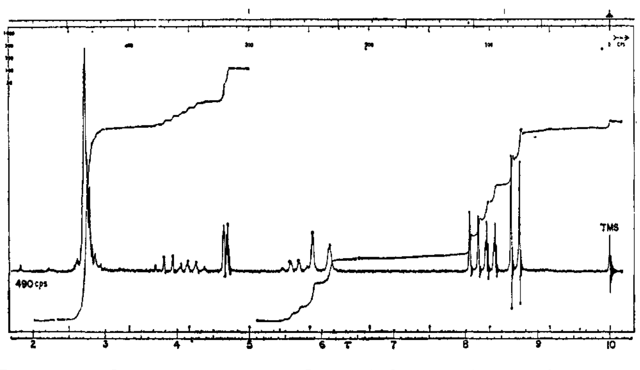
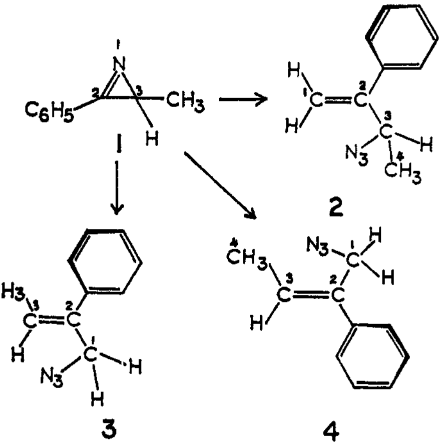


Figure 1.—Nmr spectrum (60-Mc) of the reaction product of 3-methyl-2-phenyl-1-azirine with diazomethane.

stand 3 days at room temperature, column chromatography furnished an oily product representing >21% conversion of **1**. The oil showed a single spot in thin layer chromatography using several solvent systems and had the correct analysis for $C_{10}H_{11}N_3$. The infrared spectrum showed absorption maxima at 2100 cm^{-1}, indicative of an azido grouping, at 1630 cm^{-1}, owing to C=C stretching, and at 875 and 830 cm^{-1}, suggestive of the presence of two types of double bond substitution, $C{=}CH_2$ and C=CH, respectively. The ultraviolet spectrum, λ_{max}^{EtOH} 235 mμ (ε 8650), indicated a partially conjugated phenyl grouping. The nmr spectrum in carbon tetrachloride (Figure 1) showed four distinct regions of absorption: three different methyl signals, a region of absorption indicative of proton(s) attached to carbon bearing a highly electronegative atom or group, three distinct resonances in the olefinic region, and aromatic proton signals. The mass spectrum of the oil did not show a molecular ion peak even at an electron energy of 10 eV. Prominent peaks were found at *m/e* 145 (M − 28) and 144, and that at *m/e* 28 was the most abundant in the spectrum.



The combined spectroscopic data suggested the presence in the oil of three isomeric allylic azides. Further, mechanistic considerations led to three plausible structures: 3-azido-2-phenyl-1-butene (**2**) and the stereoisomeric 1-azido-2-phenyl-2-butenes (**3**,**4**). Compounds **3** and **4** are designated as *trans* and *cis*, respectively, on the basis of the parent butene system. The data on the oil are, in fact, in excellent agreement with these structures. A detailed interpretation of the nmr spectrum was facilitated by the observation that the absorptions arising from corresponding protons or groups of protons (aromatic protons excluded) exhibited different chemical shifts for each compound. This was confirmed by double irradiation experiments. 3-Azido-2-phenyl-1-butene (**2**) showed a clean doublet, $J_{3,4}$ = 6.9 cps, at τ 8.69 (methyl protons), a ragged 1:3:3:1 quartet, $J_{3,4}$ = 6.9 cps, at τ 5.62 due to the C-3 proton, and a pair of doublets (J_{gem} = 0.8 cps) of which the higher field member is split further by allylic coupling ($J_{1,3}$ = 1.0 cps) at τ 4.69 and 4.65 due to the olefinic protons. The *trans* compound **3** exhibited methyl proton resonance as a doublet of triplets centered at τ 8.34, $J_{3,4}$ = 6.8 cps and $J_{1,4}$ = 0.8 cps, a broad singlet, $W_{1/2}$ = 3.4 cps, at τ 6.12 due to the C-1 protons, and a quartet of triplets, $J_{3,4}$ = 6.8 cps and $J_{1,3}$ = 1.0 cps, at τ 4.19 due to the olefinic proton at C-3. The *cis* compound **4** showed a doublet, $J_{3,4}$ = 6.8 cps, at τ 8.10 due to the methyl protons, a broad singlet, $W_{1/2}$ = 2.2 cps, at τ 5.87 due to the C-1 protons, and a clean quartet, $J_{3,4}$ = 6.8 cps, at τ 3.87 due to the proton at C-3. The aromatic protons for all compounds appeared as a multiplet between τ 2.93 and 2.52. The relative integrated intensities gave the composition of the oil as **2** = 44 ± 5%, **3** = **4** = 28 ± 5%.

The reason for presenting the nmr data in detail is that the spectrum not only provides the most direct proof of structure and stereochemistry but also exhibits interesting examples of shielding effects and long range spin–spin interactions which are generally instructive. Diamagnetic shielding by the phenyl group,[16-18] manifested in the different chemical shifts for the methyl groups in **3** and **4**, leads to the suggestion, supported by the ultraviolet spectrum, that the phenyl ring is twisted out of coplanarity with the C=C bond as this would minimize nonbonded interactions with the α substituents.[17] The geminal coupling constant for **2** fits well its environment both on theoretical and empirical grounds.[19] Resolvable four- and five-bond long range spin–spin interactions[20,21] were observed, and these were established by double irradiation experiments. The allylic coupling in **3** is cisoid and is 1.0 cps. The homoallylic coupling in **3** is transoid.[22]

The formation of the allylic azides is probably the result of at least a two-step process. Whether the initial addition proceeds through a highly ordered transition state with[23] or without[4] charge imbalance, and whether the triazoline adduct **5** is actually produced in the reaction as an intermediate is not known.[15] Allylic azides are said to undergo isomerization very rapidly and triazoline intermediates were proposed by Gagneux, Winstein, and Young[24] for the rapid equilibration of pentenyl and butenyl azides. A similar formulation employing the valence tautomers **5** and **5a** could be used here to account for the formation and rearrangement of the allylic azides **2**, **3**, and **4**.

The reaction of diazomethane with 3,3-dimethyl-2-phenyl-1-azirine (**6**) in ether, after 6 days at room temperature, produced the allylic azides **7** and **8**

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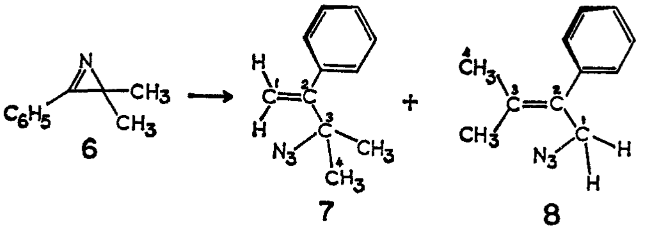
in 10% conversion and in a ratio (per cent) of 25:75 ± 10.[25] The reaction of the representative azirines 1 and 6 with diazomethane is in contrast to the reaction of 2-phenyl-1-azirine[26,27] with dimethylsulfonium methylide communicated by Hartmann and Robertson.[28] The latter combination produces an azabicyclobutane, 3-phenyl-1-azabicyclo[1.1.0]butane.



Experimental Section

3-Methyl-2-phenyl-1-azirine (1).—Propiophenone dimethylhydrazone methiodide was prepared[29] and crystallized from ethanol–ethyl acetate: mp 155–156°; yield 58%; $\nu_{\max}^{\text{Nujol}}$ 1610 cm^{-1}; nmr (DMSO-d_6, TMS) τ 8.97 (t, 3 H), 6.76 (q, 2 H), 6.33 (s, 9 H), 2.67–2.14 (m, 5 H).

Anal. Calcd for $C_{12}H_{19}IN_2$: C, 45.28; H, 5.97; N, 8.81. Found: C, 45.34; H, 5.99; N, 8.82.

A solution of 15.9 g (0.05 mol) of the quaternary hydrazone in 150 ml of dimethyl sulfoxide was treated with 2.4 g of a 51% dispersion of sodium hydride in mineral oil. The reaction mixture was stirred at room temperature for 3 hr and then poured into 700 ml of water and extracted with ether. The combined ethereal extracts were washed with water and dried ($MgSO_4$). Removal of solvent gave a yellow oil (6.2 g) which was fractionated under reduced pressure to give 4.1 g (63%) of **3-methyl-2-phenyl-1-azirine** (1)[30] as a colorless oil; bp 88° (8 mm); n^{25}D 1.5375; $\nu_{\max}^{\text{film}}$ 1730 cm^{-1} (C=N); nmr ($CDCl_3$) τ 8.68 (d, J = 4.5 cps, 3 H), 7.74 (q, J = 4.5 cps, 1 H), 2.64–2.00 (m, 5 H).

Anal. Calcd for C_9H_9N: C, 82.40; H, 6.92. Found: C, 82.38; H, 6.85.

The residue from the distillation gave, on dilution with ether, 0.28 g of 2,5-dimethyl-3,6-diphenylpyrazine as colorless prisms: mp 121–122° (lit.[31] mp 125–128°); nmr ($CDCl_3$) τ 7.37 (s, 6 H), 2.80–2.30 (m, 10 H).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.09; H, 6.17; N, 10.96.

Reaction of Azirine 1 with Diazomethane. Formation of Allylic Azides 2, 3, and 4.—A solution of 2.62 g (0.02 mol) of 1 in 20 ml of ether was treated with excess of an ethereal solution of diazomethane followed by 2 ml of methanol.[9] The reaction mixture was allowed to stand at room temperature for 3 days. The solvent was removed, and the residual oil (2.72 g) was chromatographed over silica gel to give 0.74 g (21.4%) of the mixture of **2**, **3**, and **4**, a colorless oil, as the benzene eluate. The compounds showed a single spot on silica gel plates in several solvent systems (R_f 0.625 in benzene). Most of the remaining material was the unreacted azirine **1**, which was eluted with benzene–ether. The allylic azide mixture showed $\nu_{\max}^{\text{film}}$ 2100, 1630, 875, 830 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 235 mμ (ϵ 8650); the nmr spectra in CCl_4 (Varian A60 and HA 100 instruments) showed absorptions of chemical shift, area, and splitting patterns described in the Discussion (see also Figure 1).

Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26; mol wt, 173.21. Found: C, 69.39; H, 6.48; N, 24.44; mol wt, 179 (osmometric in benzene).

Reaction of Azirine 6 with Diazomethane.—A solution of 1.45 g (0.01 mol) of 3,3-dimethyl-2-phenyl-1-azirine (6)[2,29] in 20 ml of ether was treated with diazomethane in ether over a period of 2 days. The reaction mixture was allowed to stand at room temperature for 4 days, then worked up and chromatographed as described above to give 0.195 g (10.4%) of a mixture of **3-azido-3-methyl-2-phenyl-1-butene** (7) and **1-azido-3-methyl-2-phenyl-2-butene** (8) in addition to 1.29 g of unreacted starting material (6). Thus, the yield was nearly quantitative if based on unrecovered starting material. Product analysis was carried out by nmr spectroscopy: nmr (CCl_4) τ 8.63 (methyls of **7**), 8.33 and 8.08 (methyls of **8**), 6.00 (C-1 protons of **8**), 4.88 and 4.60 (C-1 olefinic protons of **7**), 2.90–2.53 (aromatic protons).

Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00. Found: C, 70.89; H, 7.09.

Registry No.—**1,** 16205-14-4; **2,** 16205-15-5; **3,** 16223-64-6; **4,** 16205-16-6; **7,** 16205-17-7; **8,** 12605-18-8; diazomethane, 334-88-3.

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Azetidines. III.[1] A Convenient Synthesis of 1-Alkyl-3,3-dimethylazetidines[2,3]

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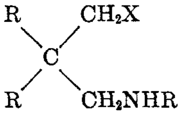
In the course of studies on tertiary and quaternary derivatives of azetidines,[1] need arose for a convenient synthesis for 1-substituted 3,3-dimethylazetidines. The method that was developed is described in this paper.

Consideration of the elegant route to 3-substituted azetidines *via* lithium aluminum hydride reduction of β-lactams[4] and malonimides[5] revealed that the use of N-substituted compounds gave ring cleavage to the corresponding aminopropanol.[6] Thus formation of a secondary azetidine, acylation, and then a second hydride reduction was required to obtain a tertiary azetidine.[7] A more direct route was therefore sought.

The acyclic structure (1) appeared to be favorable as a precursor as side reactions such as bimolecular substitution and elimination would be hindered or precluded, respectively. Also no examples of fragmentation[8] were found for acyclic compounds in which halogen



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