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Azimines Revisited: The Structure of a Magenta Dye[1]

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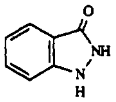
The dye formed on condensation of *N,N*-diethyl-4-nitrosoaniline with indazolin-3-one is shown by X-ray crystallography to have the azimine structure **7b**.

History

Nearly 40 years ago, J. J. Jennen, at the laboratories of Gevaert, Antwerp, found that indazolin-3-one (1) behaved as an effective "color former" in the presence of *p*-(dimethylamino)aniline and a silver oxidant.[2] His intention had been to develop new fused pyrazolinones with (potential or actual) active methylene groups, many of which had been found to form useful colors in the way described. The indazolinone was the product of an unsuccessful synthesis, and the formation of a dye from a material that did not contain the requisite methylene group was somewhat surprising.



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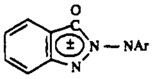

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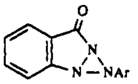

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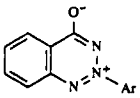

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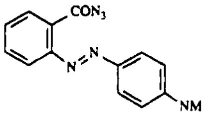

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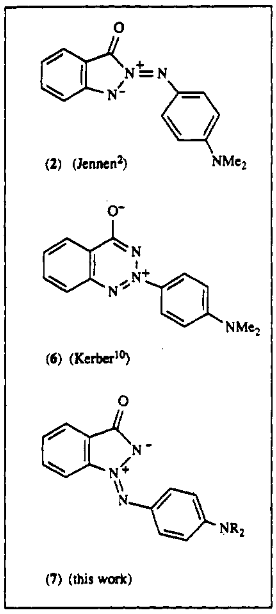
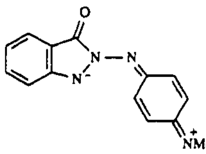


(2) (Jennen[2])

(6) (Kerber[10])

(7) (this work)



(2a)

The color that is produced is remarkably stable: dilute solutions, prepared in ethanol or dichloromethane for UV/vis spectral measurements, show no sign of alteration or fading after several months of exposure to light on an open bench, although, exceptionally, carbon tetrachloride solutions in sunlight show evidence of fairly rapid decomposition. It is strikingly solvatochromic, which no doubt accounts for its several descriptions by Jennen and others as magenta, blue, and purple-red. Jennen assigned the structure 2 to this product.

In a second paper,[3] 5 years later, Jennen discussed the mechanism of formation of structure 2 and described a more convenient preparation by condensation of indazolinone with *p*-nitrosodimethylaniline. Patents and other publications,[4–7] reporting modifications to the indazolinone structure and using *p*-nitrosodiethylaniline in place of the dimethyl compound, appeared in the meantime, and subsequently.

2-(Arylimino)indazolone structures appeared again in the literature, very shortly after Jennen's original report claiming structure 2, in the course of a proposed revision of the structures of Chattaway's compounds.[8] These rather unstable materials, the oxidation products of *o*-nitrobenzaldehyde arylhydrazones, can be reduced to a parallel series of much stabler compounds containing one atom of oxygen fewer. The reduction products were suggested by Gibson[9] to have structure 3, rather than the fused triaziridine system 4, which had originally been proposed by Chattaway.

Some years later, Kerber[10] reinvestigated Chattaway's compounds and pointed out that their spectral data and mode of formation were more consistent with 2-aryl-1,2,3-benzotriazinone betaine 1-oxide structures and that the reduced compounds should be the 2-arylbetaines **5**. Later workers[11,12] established beyond doubt that this revision was correct. Kerber also looked into Jennen's claims

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[1] The crystal structure determinations described in this paper were carried out independently in Norwich and Antwerp, and the results were submitted practically simultaneously to this journal. The present paper of joint authorship was written to avoid duplication of publications.

[2] Jennen, J. J. *Ind. Chim. Belge* **1951**, *16*, 472–474; *Chem. Abstr.* **1952**, *46*, 6387.

[3] Jennen, J. J. *Mededel. Vlaam. Chem. Ver.* **1956**, *18*, 43–58; *Chem. Abstr.* **1957**, *51*, 5094.

[4] Jennen, J. J. U.S. Patent 2 673 801, 1954; *Chem. Abstr.* **1954**, *48*, 9850.

[5] Jennen, J. J.; Eerdekens, H. P. U.S. Patent 2 964 402, 1960; *Chem. Abstr.* **1961**, *55*, 9129.

[6] Chernokal'skii, B. D.; Groisberg, A. T.; Bezdenezhnaya, A. A. *Khim. Geterotsikl. Soedin., Akad. Nauk Latv. SSSR* **1965**, 412–415; *Chem. Abstr.* **1965**, *63*, 16 332.

[7] Coraluppi, E.; Magagnoli, R. Fr. Patent 1 516 610, 1968; *Chem. Abstr.* **1969**, *71*, 71932; *Idem.* U.S. Patent 3 486 894, 1969; *Chem. Abstr.* **1970**, *72*, 122949.

[8] For a review of the older literature, see: Erikson, J. G. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1956; Vol. 10, p 27.

[9] Gibson, M. S. *Nature* **1962**, *193*, 474; *Tetrahedron* **1962**, *18*, 1377.

[10] Kerber, R. C. *J. Org. Chem.* **1972**, *37*, 1587–1592.

[11] McKillop, A.; Kobylecki, R. J. *J. Org. Chem.* **1974**, *39*, 2710–2714.

[12] Ballard, R. E.; Norris, E. K. *Acta Crystallogr., Sect. B*, **1975**, *31*, 626–628.

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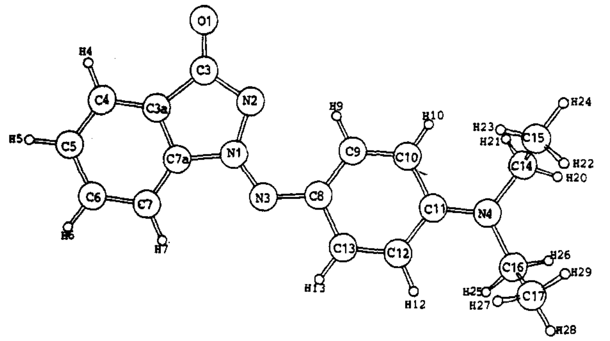

Figure 1. Structure of the dye 3*H*-indazol-3-one 1-[4-(diethylamino)phenyl]imine (**7b**) in the crystal.

again. On the basis of infrared and mass spectral similarities with Chattaway's (reduced) products, he proposed that Jennen's dye be assigned the benzotriazinone betaine structure **6**. He suggested that the initial condensation of the nitroso group with the indazolinone was more likely to take place at the 1- rather than the 2-position, but the azimine **7** so formed could rearrange via the triaziridine **4** to form the betaine **6**. The formation of (a very small amount of) the dye by decomposition of 2-[[4′-(dimethylamino)phenyl]azo]benzoyl azide (**8**)[13] was considered to be supporting evidence for structure **6**.

Although some doubt has been cast upon structure **6**, on unspecified (presumably ultraviolet) spectral grounds,[14] Kerber's views have not so far been effectively challenged. However, workers in the dyestuff and photographic color area seem to have paid little or no attention to them, and Jennen's structure **2** has continued to be favored, despite the fact that is seems to be the least appealing of all the various isomeric possibilities. (A 2-acylazimine should be very susceptible to rearrangement to the 3-acyltriazene system, in the present instance forming the 3-arylbenzotriazinone **9**.[15]) Thus, Klicnar et al.[16] investigated the IR spectra of indazolinones and several of their derivatives, and they considered that their results "proved spectroscopically" the "quinoid structure of the dyestuff prepared from 3-indazolinone and *N*,*N*-dimethyl-*p*-nitrosoaniline", for which they drew the formula **2a**. Textbooks[17] continue to quote Jennen's structure **2**, without reference to Kerber's work.

Results and Discussion

An indication (which later proved to be spurious) that Kerber's structure **6** for the indazolinone–*p*-nitrosodimethylaniline product could not be correct was found when we treated indazolinone (**1**) with nitrosobenzene. As with the nitrosodimethylaniline reaction, a magenta-purple material was formed with UV and solvatochromic characteristics very similar to those of Jennen's compound. It evidently could not be the analogue **5** (Ar = Ph) of Kerber's formula, however, because this is a known compound, pale yellow in color.[11]

Table I. Bond Lengths (Å)[a] and Selected Angles (deg)[b] in Structure 7b

bond	length	bond	length	bonds	angle
N1–N2	1.368 (3)	N4–C16	1.479 (3)	N1–N2–C3	105.6
N2–C3	1.381 (3)	C16–C17	1.486 (5)	N2–C3–C3a	109.5
C3–O1	1.229 (3)	C4–H4	0.957 (31)	N2–C3–O1	123.4
C3–C3a	1.480 (4)	C5–H5	1.010 (32)	C3–C3a–C7a	106.1
C3a–C4	1.378 (4)	C6–H6	1.001 (32)	C7a–N1–N2	112.4
C4–C5	1.381 (4)	C7–H7	0.979 (31)	N2–N1–N3	128.6
C5–C6	1.398 (4)	C9–H9	0.968 (31)	N3–C8–C9	129.8
C6–C7	1.383 (4)	C10–H10	0.968 (32)	N3–C8–C13	113.7
C7–C7a	1.371 (4)	C12–H12	0.998 (31)	C9–C8–C13	116.5
C3a–C7a	1.378 (3)	C13–H13	0.977 (32)	C10–C11–C12	116.3
N1–C7a	1.428 (3)	C14–H20	1.026 (35)	C10–C11–N4	120.8
N1–N3	1.288 (3)	C14–H21	1.050 (34)	C12–C11–N4	122.9
N3–C8	1.368 (3)	C15–H22	1.023 (34)	C11–N4–C14	121.7
C8–C9	1.406 (4)	C15–H23	0.993 (36)	C11–N4–C16	121.5
C9–C10	1.358 (4)	C15–H24	1.042 (35)	C14–N4–C16	116.8
C10–C11	1.423 (3)	C16–H25	1.054 (34)		
C11–C12	1.414 (4)	C16–H26	1.077 (35)		
C12–C13	1.360 (4)	C17–H27	1.043 (35)		
C8–C13	1.417 (3)	C17–H28	0.954 (35)		
C11–N4	1.349 (3)	C17–H29	0.999 (35)		
N4–C14	1.466 (4)				
C14–C15	1.514 (5)	N2–H9[c]	2.170 (31)		

[a] esds in parentheses. [b] For all angles quoted, esd value was 0.2°. [c] Nonbonded distance.

We found isolation and purification of the nitrosobenzene product to be difficult,[18] and therefore we sought a well-crystalline derivative for study. The *p*-nitrosodiethylaniline product, originally described by Chernokal'skii et al.[6] in 1965, proved suitable. Bond lengths and angles are listed in Table I, and Figure 1 shows the configuration of the molecule in the crystal. Jennen's dye is thus unequivocally demonstrated to have structure **7**, rather than **2**, as proposed originally by Jennen, or **6**, as suggested by Kerber.

The dye **7b** is essentially planar in the crystal, including the α-carbon atoms of the ethyl groups; the β-carbons are twisted from the plane. Interaction between N2 and an ortho hydrogen (H9) of the phenylene ring slightly distorts the N3–C8 bond, so that it makes an angle of 8° with the bisector of the exterior angle at C8. There is a small degree of bond variation in the phenylene ring, which may imply a contribution from the quinonoid structure. The benzo-fused (indazole) ring has regular, practically nonalternating bond lengths, while the two bonds N1–C7a and C2–C3a in the heterocyclic ring are long.

The structure **7** has been considered before[10] as an intermediate to the betaine **6**. It is, in fact, the only simple alternative (to **6**) that could be formed from the decomposition of Kerber's azide **8** without involving a Curtius rearrangement. However, since the major product of that reaction has the (rearranged) structure **9**, the reaction does not provide a great deal of support for **7**. A group of indazolinone-derived dyes with azomethine imine structures were developed at Kodak in the early 1960s.[19] Described as "holopolar", they were formed by condensation of a polymethine chain to the indazolinone 1-position, as in structure **12**, in a clear analogy to **7**.

Although Jennen's original procedure[2] (AgCl oxidation of a mixture of indazolinone (**1**) and *p*-amino-*N*,*N*-dimethylaniline) formed the dye efficiently, we could detect no trace of a similar purple product on oxidation of *p*-

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(13) Kerber, R. C.; Heffron, P. J. *J. Org. Chem.* **1972**, *37*, 1592–1597.

(14) McKillop, A.; Kobylecki, R. J. *Adv. Heterocycl. Chem.* **1976**, *19*, 234.

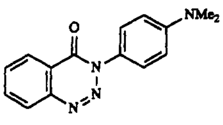
(15) (a) An analogy to the 2-acylazimine system—the deep yellow or orange 2-(arylimino)-1,2,4-triazol-3-ones **10**—has been described by G. V. Boyd and co-workers.[15b] Rearrangement to the isomeric 1,2,3,5-tetrazinones **11** is proposed, but apparently only on the grounds of identical decomposition products and mass spectra. (b) Baydar, A. E.; Boyd, G. V.; Lindley, P. F.; Walton, A. *J. Chem. Soc., Chem. Commun.* **1982**, 225–226.

(16) Klicnar, J.; Olbrachtová-Nyklová, B.; Šlosar, J.; Šlosar, P.; Večeřa, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 327–337.

(17) E.g., Fleckenstein, L. J. In *The Theory of the Photographic Process*, 4th ed.; James, T. R., Ed.; Collier-Macmillan: London, 1977; p 358. Bailey, J.; Clark, B. A. J. In *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon: Oxford, 1984; Vol. 1, p 372.

(18) The structure of this product is still under investigation.

(19) Webster, F. G.; Brooker, L. G. S. U.S. Patent 2 961 317, 1960; *Chem. Abstr.* **1961**, *55*, 6221.



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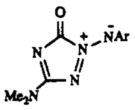

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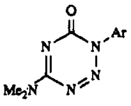

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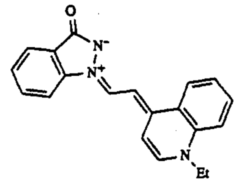

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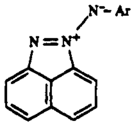

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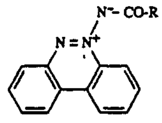

(14)

anisidine in the presence of 1. In the Experimental Section we describe a modification of the nitrosoaniline route to dye 7 and its congeners, which has been found to be superior to the methods previously used.

Pariser–Parr–Pople (PPP) calculations were carried out on the structure 7, using the dimensions given in Figure 1.[20] The longest wavelength transition was thus predicted to arise at 515 nm, compared with a found value (in EtOH) of 548 nm.[10] Other azimines that have been described are yellow or orange; exceptions, and the deepest colors noted to date, are the dark red-violet *N*-(arylimino)benz[*cd*]indazoles 13 of Spagnolo et al.,[21] which absorb, like the azimines 7, in the region 540–560 nm. Rees and coworkers[22] investigated a series of benzo[*c*]cinnoline *N*-imines, including the acyl derivatives 14, a model for structure 7 with a carbonyl group at the terminal azimine nitrogen, but these also were yellow (λ_{max} 434 (R = Ph), 414 nm (R = Me)). Therefore, although there is some precedent, and justification in theory, for the colors of the azimines 7, they do appear rather anomalous when compared with the majority of analogues that are known.

Experimental Section

General Procedure for Synthesis of 3*H*-Indazol-3-one 1-[4-(Dialkylamino)phenyl]imines (Magenta Dyes 7). The 4-nitroso-*N*,*N*-dialkylaniline or its salt (4 mol) in triethylamine (2.85 L) was stirred for 15 min. Acetone (4 L) was added, and the solution was heated to reflux. 3-Indazolinone (1; 720 g, 5.3 mol) was added in three portions at 3-h intervals, and the mixture was refluxed for a further 20 h. After the mixture was cooled to room temperature, the precipitated salt was filtered off and washed with acetone (1.8 L). The filtrate was cooled to 0 °C and allowed to crystallize. The product 7 was filtered off, washed consecutively with *n*-hexane/acetone (20:1; 1.1 L) and *n*-hexane/acetone (40:1; 1.1 L), and dried at 50 °C. Yields varied from 50–75%.

7a (R = CH_3): small reddish purple prisms or needles from propanol, mp 229 °C (lit.[2] mp 198° for compound assigned as structure 2); UV λ_{max} 543 nm ($\log_{10} \epsilon = 4.85$, MeOH); MS (70 V ei) *m*/*z* 267 (18, $P^+ + 1$), 266 (100, P^+), 265 (12), 136 (15), 134 (20), 133 (16), 120 (49), 119 (17), 105 (29), 79 (14), 78 (13), 77 (26), 42 (29). The EI-MS of compound 7a was identical with that of the benzotriazinone 9;[3,13] all other spectral data, and the melting points of the two compounds, were completely different. Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.6; H, 5.2; N, 21.0. Found: C, 67.3; H, 5.4; N, 20.8.

Compound **7b** (R = Et) was further purified by column chromatography (CH_2Cl_2/methanol (20:1)) and recrystallized from 1-propanol to obtain deep red-purple prisms with metallic green reflection: mp 182 °C (lit.[6] mp 179–180 °C); UV λ_{max} (solvent) 565 (H_2O), 551 ($\log_{10} \epsilon = 4.91$, MeOH), 551 (EtOH), 545 ($CHCl_3$), 536 nm (hexane); IR ν_{max} 1655 (C=O), 1595, 1285, 1140, 1075, 1045, 820, 765, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.56 (2 H, M, J_{AB} = 9.6 Hz, *AA*′BB′), 7.91–7.5 (4 H, m, ABCD), 6.71 (2 H, m, *J* = 9.6 Hz, AA′*BB*′), 3.49 (4 H, q, *J* = 7 Hz, NCH_2CH_3) and 1.25 (6 H, t, *J* = 7 Hz, NCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 176.8 (C3), 151.2, 147.7, 134.8, 125.4 (C3a, C7a, Cl′, C4′), 134.1 (C2′/6′), 131.0 (C7), 130.4 (C4), 122.9 (C6), 114.1 (C5), 111.1 (C3′/5′), 45.1 (NCH_2CH_3), 12.7 (NCH_2CH_3); MS (70 V ei) *m*/*z* 295 (24, $P^+ + 1$), 294 (92, P^+), 280 (28), 279 (100, $P^+ - CH_3$), 266 (23), 162 (21), 149 (22), 147 (40), 133 (20), 105 (25). Anal. Calcd for $C_{17}H_{18}N_4O$: C, 69.4; H, 6.2; N, 19.0. Found: C, 69.4; H, 6.1; N, 18.7.

7c (R = *n*-C_3H_7): prisms, green by reflected, red by transmitted, light; mp 162 °C; UV λ_{max} 553 nm ($\log_{10} \epsilon = 4.93$, MeOH). Anal. Calcd for $C_{19}H_{22}N_4O$: C, 70.8; H, 6.9; N, 17.4. Found: C, 70.9; H, 6.8; N, 17.3%.

7d (R = *n*-C_4H_9): violet prisms, red by transmitted light: mp 114 °C; λ_{max} 555 nm ($\log_{10} \epsilon = 4.925$, MeOH). Anal. Calcd for $C_{21}H_{26}N_4O$: C, 72.0; H, 7.5; N, 16.0. Found: C, 72.15; H, 7.5; N, 16.0%.

7e (R = C_2H_4OH): slate-blue, highly refractive needles, mp 180 °C; UV λ_{max} 545 nm ($\log_{10} \epsilon = 4.87$, MeOH). Anal. Calcd for $C_{17}H_{18}N_4O_3$: C, 62.6; H, 5.6; N, 17.2. Found: C, 62.8; H, 5.5; N, 16.9%.

X-ray Structural Analysis of 7b. Diffraction measurements were made on a Nicolet P3 four-circle diffractometer. The crystal class, orientation matrix, and accurate unit cell parameters were determined using a least-squares procedure involving 20 centered reflections with 8° < 2θ < 25°.

Crystal Data: Compound **7b**, $C_{17}H_{18}N_4O$, M = 294.36, monoclinic, $a = 9.281$ (3) Å, $b = 14.016$ (6) Å, $c = 12.267$ (6) Å, $\beta = 102.44$ (3)°, $V = 1558.4$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $F(000) = 624$, space group $P2_1/n$, Mo K_α radiation, $\mu = 0.076$ mm^{-1}.

Intensities for a crystal of dimensions 0.50 × 0.32 × 0.30 mm for 3350 reflections ($\pm h,k,l$) were measured at 23 °C using the $\omega - 2\theta$ variable-scan (1.50–14.65° min^{-1}) technique in the bisecting mode up to $2\theta_{max} = 52°$.

The structure was solved using direct methods and refined by full-matrix least-squares techniques with anisotropic temperature factors for all non-hydrogen atoms using the Shelx programs.[27] Atomic scattering factors were obtained from ref 28. Hydrogen atoms were located from Fourier difference maps and refined with fixed temperature factors. Convergence for 2050 observed data with $F > 6\sigma F$ and 253 variables was reached at $R = 0.047$ (unit weights). The largest peak in the final electron density map is 0.18 e Å^{-3} and the largest hole 0.19 e Å^{-3}. The structure so revealed is shown in Figure 1, and the bond lengths and angles are listed in Table I.

A second structure determination was carried out using an Enraf-Nonius CAD4 diffractometer, after application of MULTAN (1971),[29] solving using Enraf-Nonius CAD4-SDP[30] on a Microvax

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II (DEC, VMS) computer. Final convergence was reached at R = 0.041, R_w = 0.037. The maximum noise level in the final difference Fourier was 0.16 e Å^{-3}. The bond lengths and angles differed in no substantial detail from those revealed by the first determination. Structure factor data from both laboratories and detailed tables of the molecular dimensions are available as supplementary material.

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Registry No. 1, 7364-25-2; **7a**, 134905-26-3; **7b**, 134905-27-4; **7c**, 134905-28-5; **7d**, 134905-29-6; **7e**, 134905-30-9.

Supplementary Material Available: Tables of crystallographic data and positional parameters from both research groups; ^{1}H (at 90 MHz) and ^{13}C NMR spectra (22.5 MHz) for compound **7b** (7 pages). Ordering information is given on any current masthead page. Tabulated *F* values are filed with the Cambridge Crystallographic Data Centre.

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A Novel Approach to Angular Triquinanes via Intramolecular 1,3-Dipolar Cycloaddition of Nitrile Oxide

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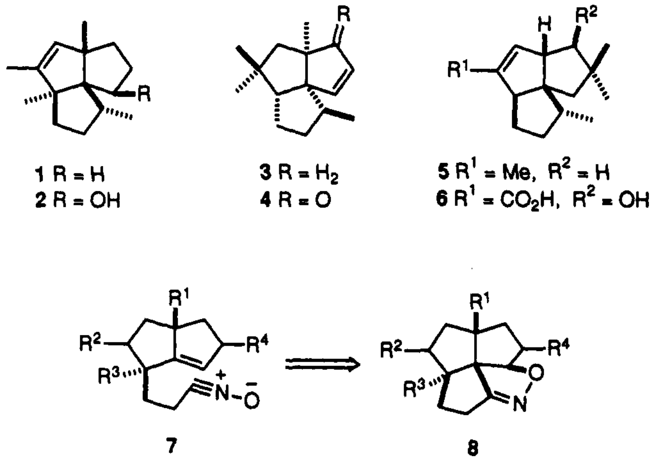
The framework of angular triquinane sesquiterpenes was stereoselectively constructed via the intramolecular 1,3-dipolar cycloaddition of nitrile oxide precursors. Optically active indandione **9** was converted into olefinic oximes **18A** and **18B** through two successive alkylations, followed by ring contraction. Oxidation of the mixture **18A** and **18B** with sodium hypochlorite gave rise to tetracyclic isoxazolines **21A** and **21B**, which were transformed into tricyclo[6.3.0.0^{4,8}]undecanes **28** and **29**.

Introduction

Angular-type triquinane sesquiterpenes, represented by isocomene (**1**), silphinene (**3**), and pentalenene (**5**), have received a great deal of attention from synthetic chemists due to their unique architectural features.[1] Recently we synthesized (±)-3-oxosilphinene (**4**) via intramolecular Diels–Alder reaction[2] and (±)-pentalenene (**5**) and (±)-pentalenic acid (**6**) via an intramolecular double Michael reaction (Scheme I).[3] It was considered that the intramolecular 1,3-dipolar cycloaddition of nitrile oxide **7** giving tetracyclic isoxazoline **8** could provide an useful route to angular triquinanes. Although extensive studies of 1,3-dipolar cycloadditions have been carried out,[4] few examples of construction of spiro ring systems using intramolecular 1,3-dipolar cycloadditions of nitrile oxides or nitrones have been recorded.[5] The 1,3-dipolar cycloaddition of nitrile oxide **7**, which could be prepared from the optically active indandione **9**,[6] was thus investigated. We wish to report

Scheme I



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