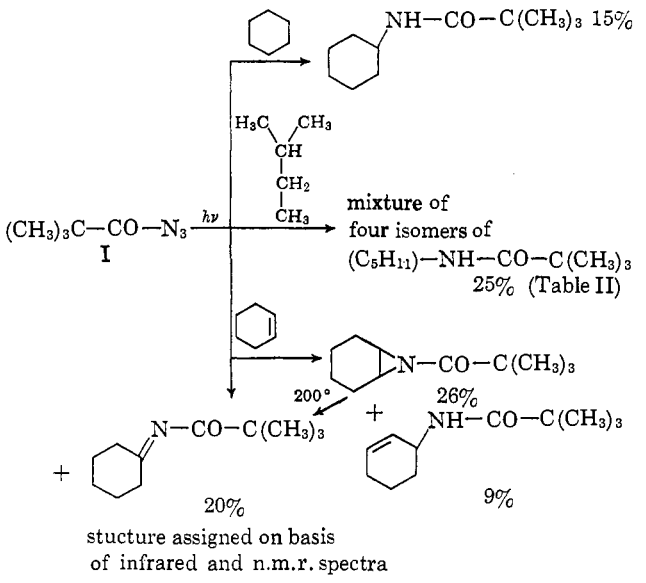
t-butyl isocyanate (*t*-Bu–NCO). With our analytical methods we would have detected a 1% yield of insertion or addition products. However, photolysis of solutions of I in cyclohexene, cyclohexane, or 2-methylbutane with a medium pressure mercury lamp at −15 to +5° gave, in addition to *t*-butyl isocyanate, a spectrum of products best explained as arising from the insertion of pivaloyl nitrene into C–H bonds or its addition to double bonds. Chart I shows these inter-

Chart I. Products from Cyclohexene and Cyclohexane



Structure assigned on basis of infrared and n.m.r. spectra

molecular products, Table I the relative reactivities of the intermediate with the three kinds of C–H bonds in 2-methylbutane. In this solvent, insertion into the tertiary, secondary, and the two types of primary C–H bonds took place. The four isomeric isopentylpivalamides were synthesized from the corresponding amines and the synthetic compounds used for identification (by v.p.p.c. retention time and infrared and n.m.r. spectra) and for calibration of the vapor phase partition chromatograph.[14] In the photolysis of I, the isopentyl pivalamides were formed in a total yield of 25%, indicating that at least that much of the azide I is converted to the selective intermediate.

Table I. Reactivities of the C–H Groups in 2-Methylbutane toward Pivaloyl Nitrene (corrected for the number of hydrogens)

	Type of C–H bond		
	Tertiary	Secondary	Primary
Rel. reactivity	160	8.6	1
Rel. error	±25%	±12%	..

Photolysis in cyclohexane gave N-cyclohexylpivalamide, photolysis in cyclohexene the allylic C–H insertion product plus products from addition to the double bond, as shown in Chart I. The products were identified by comparison of their v.p.p.c. retention times and infrared and n.m.r. spectra with those of samples prepared by independent, unequivocal syntheses.[14]

The qualitative similarity of the reactions observed here to those of carbethoxy nitrene[3] make us inclined to think that pivaloyl nitrene, *t*-Bu–CO–N, is the reactive intermediate in the intermolecular reactions. Since thermal decomposition of I did not give unrearranged intermolecular products, the same intermediate cannot be involved in the thermal rearrangement, which might proceed in a concerted fashion or perhaps through a different intermediate. This question is currently being studied in our laboratory.

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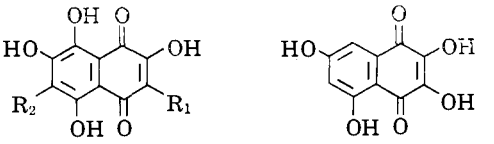
The Synthesis of Spinochromes A, C, D, and E

Sir:

Investigation of the pigments derived from the spines of sea urchins began in 1885[1] and for many years the literature in the field abounded in unsubstantiated structural proposals of at least twelve presumably distinct compounds. As a result of recent researches this number has been reduced to six pigments of unquestioned identity. They are echinochrome A (**1**) and spinochromes A (**2**), B (**3**), C (**4**), D (**5**), and E (**6**). The structure of echinochrome A



3

1, $R_1 = C_2H_5$; $R_2 = OH$
2, $R_1 = COCH_3$; $R_2 = H$
4, $R_1 = COCH_3$; $R_2 = OH$
5, $R_1 = OH$; $R_2 = H$
6, $R_1 = OH$; $R_2 = OH$

was unambiguously demonstrated by synthesis more than 20 years ago.[2] The nature of the spinochromes had remained obscure until Thomson established the structures of D[3] and E[4]; Sutherland unraveled the structural tangle of B[5]; and work in this laboratory resulted in structural elucidation of A and C.[6,7] Failure to achieve clean separation of the pigments on calcium carbonate columns coupled with heavy reliance on combustion data often led to serious misinterpretation. Structural proof by synthesis is therefore needed to remove any remaining elements of doubt. This was achieved for spinochromes B (then

(14) All new compounds gave satisfactory elemental analyses. The small v.p.p.c. peaks of the primary and secondary insertion products were rather broad, causing the large relative errors noted in Table II.

(1) The early work has been reviewed by R. H. Thomson in "Comparative Biochemistry," Vol. 3, M. Florkin and H. S. Mason, Ed., Academic Press, Inc., New York, N. Y., 1962, pp. 631–725.
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designated N)[8] and D.[3] We now wish to report a convenient synthesis of spinochrome D as well as syntheses of the remaining spinochromes of established identity, A, C, and E, not previously synthesized.

Condensation of 1,2-dihydroxy-3,4-dimethoxybenzene and chloromaleic anhydride in an aluminum chloride–sodium chloride melt produced a 50% yield of a 1:2:1 mixture of 2,3-dihydroxynaphthazarin, 2,3-dihydroxy-6-chloronaphthazarin, and 2,3-dihydroxy-6,7-dichloronaphthazarin. The crude mixture was methylated with diazomethane and separation of the dimethyl derivatives was achieved by thick-layer chromatography on silica gel to yield 2,3-dimethoxynaphthazarin, m.p. 136–137° (lit.[9] m.p. 133.5°), 2,3-dimethoxy-6-chloronaphthazarin (**7**), m.p. 134–135°, and 2,3-dimethoxy-6,7-dichloronaphthazarin (**8**), m.p. 204–205°. Nucleophilic displacement of chlorine with methoxide converted **7** to 2,3,6-trimethoxynaphthazarin, m.p. 161–162°, in 42% yield (lit.[10] m.p. 160°); ultraviolet spectrum[11]: λ_{max} 317, 472, 497, and 530 mμ; n.m.r. spectrum: C-2, C-3, and C-6 methoxyl, δ 3.86, 3.98, and 4.06; C-7 hydrogen, 6.30; C-5 and C-8 hydroxyl, 12.86 and 12.98. Finally, hydrolysis of 2,3,6-trimethoxynaphthazarin in hydrobromic acid at reflux afforded *spinochrome D*, subl. 280–290° without melting, identical in all respects with an authentic sample; ultraviolet spectrum in acidic methanol: λ_{max} 330, 462, 490, and 527 mμ.

2,3-Dimethoxy-6,7-dichloronaphthazarin (**8**) was obtained as described above or, more readily and in 75% yield, by condensing 1,2-dihydroxy-3,4-dimethoxybenzene with dichloromaleic anhydride in an aluminum chloride–sodium chloride melt followed by methylation of the resulting 2,3-dihydroxy-6,7-dichloronaphthazarin, m.p. 256–257°, with diazomethane. Compound **8** was allowed to react with methoxide to yield 34% of 2,3,6-trimethoxy-7-hydroxynaphthazarin (**9**), m.p. 134–135°; ultraviolet spectrum: λ_{max} 333, 460, 490, and 522 mμ; n.m.r. spectrum: C-2, C-3, and C-6 methoxyl, δ 4.04, 4.08, 4.16; C-7 hydroxyl, 6.90 (broad); C-5 and C-8 hydroxyl, 12.16 and 13.30. Methylation of **9** with diazomethane yielded 2,3,6,7-tetramethoxynaphthazarin, m.p. 185–186° (lit.[8] m.p. 185°); n.m.r. spectrum: C-2, C-3, C-6, and C-7 methoxyl, δ 4.10; C-5 and C-8 hydroxyl, 12.68. Hydrolysis of **9** in hydrobromic acid at reflux gave *spinochrome E*, subl. 300–320° without melting, identical in every respect with the natural pigment; ultraviolet spectrum in acidic methanol: λ_{max} 358, 455 (sh), 475, and 508 (sh) mμ.

Methoxynaphthazarin, m.p. 195–196° (lit.[12] m.p. 178°), obtained in 82% yield from chloronaphthazarin and methoxide, was oxidized to 2-methoxy-1,4,5,8-naphthodiquinone with lead tetraacetate in benzene and the crude diquinone was acetylated by the Thiele method. Mild hydrolysis with ethanolic hydrochloric acid furnished a 20% yield of 6-methoxy-2-hydroxynaphthazarin, m.p. 265–267° (λ_{max} 311, 465, 493, 521, and 529 mμ), and a 55% yield of 7-methoxy-2-hydroxynaphthazarin (**10**), m.p. 240–241° (λ_{max} 313, 488, 504 (sh), 518, 538 (sh), and 555 mμ), readily separable by chromatography on silica gel. Compound **10** was then reductively acetylated to 1,2,4,5,8-pentaacetoxy-7-methoxynaphthalene, m.p. 222–223°. Treatment with boron trifluoride in acetic acid followed by mild acid hydrolysis in the presence of air converted the leucoacetate to 2,7-diacetyl-3,6-dihydroxynaphthazarin (**11**), m.p. 237–238°, in 20% yield; ultraviolet spectrum: λ_{max} 318, 531, 564, and 615 mμ; n.m.r. spectrum: C-2 and C-7 acetyl, δ 2.85; mass spectrum: *m/e* 306. Further careful acid hydrolysis of **11** resulted in the removal of one acetyl group to yield *spinochrome A* (50%), identical with the natural product.

To produce spinochrome C, the leucoacetate of D, m.p. 212–213° (lit.[13] m.p. 210°), was treated with boron trifluoride in acetic acid, followed by mild acid hydrolysis in the presence of air. After chromatography *spinochrome C* (5%), which was identical with the natural pigment, was obtained.

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(14) Grantee of the East–West Center.
(15) N.D.E.A. Fellow, 1960–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

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The Photosensitized Reaction of Dichloromaleic Anhydride with Benzene. A Novel Variation in the Photochemistry of Maleic Anhydride Derivatives

Sir:

Maleic anhydride undergoes photosensitized addition to benzene[1–3] to form the tricyclic dianhydride, Ia, while both methyl- and dimethylmaleic anhydride cyclodimerize under similar conditions.[4,5]

In an attempt to determine which course dichloromaleic anhydride (DCMA) follows, we have discovered a third and unexpected variation in the photochemistry of maleic anhydride derivatives in which a 2:2 benzene–anhydride adduct is the major product isolated. Irradiation[6] of DCMA (0.2–0.4 *M*) in benzene solutions containing benzophenone (0.2–0.4 *M*)

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