at this temperature and subsequently treated with solid ammonium chloride. Evaporation of the ammonia was followed by the addition of water and ether extraction. The customary work-up afforded a yellow oil, purification of which by preparative vpc (10% SE-30, 150°) afforded 56 mg (17%) of **14**: $\nu_{max}^{CCl_4}$ 1727 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 9.66 (t, J = 2 Hz, 1, CHO), 7.0–7.7 (m, 4, aryl), 3.82 (d, J = 2 Hz, 2, CH_2CHO), and 3.30 (s, 1, C≡CH).

The semicarbazone of **14** was obtained as a fawn-colored solid, mp 183–184° dec, from ethanol.

Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.51; N, 20.88. Found: C, 65.40; H, 5.47; N, 20.58.

Registry No.—**5**, 1487-99-6; **6**, 28362-73-4; **7**, 28362-74-5; **12**, 264-13-1; **13**, 28362-76-7; **13** semicarbazone, 28362-77-8; **14**, 28362-78-9; **14** semicarbazone, 28362-79-0; **16**, 22545-12-6; **16** 3,5-dinitrobenzoate, 22532-40-7.

Acknowledgment.—The authors are indebted to the National Institutes of Health for partial financial support of this research.

Thermally Disallowed Valence Tautomerization of an Indano[1,2-*b*]aziridine to an Isoquinolinium Imine[1a,b]

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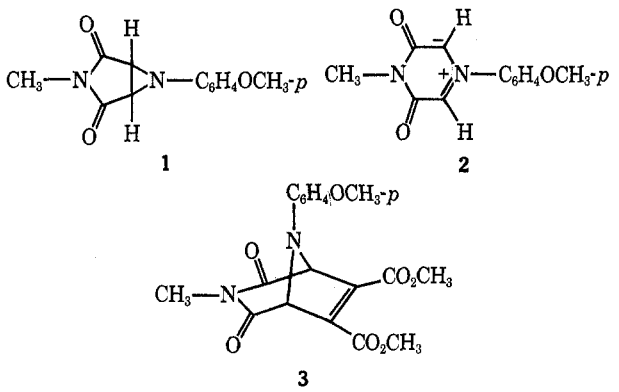
1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine (**4**) at 135° in toluene undergoes conversion to an aromatic valence tautomer, the red isoquinolinium imine **5**, despite the geometrical restrictions imposed by the molecule on the formally required conrotatory opening. Both the thermal and analogous photochemical isomerizations are reversible. The chemistry of **5** is discussed, in particular its trapping as an azomethine ylide in a series of 1,3-dipolar cycloadditions.

The thermal conrotatory opening of the cyclopropyl anion to the allyl ion predicted by the Woodward–Hoffman rules[2] has yet to receive experimental verification. However, Huisgen and his coworkers have convincingly demonstrated both the expected thermal conrotatory and photochemical disrotatory opening of examples of the isoelectronic analog aziridine to azomethine ylides.[3] Subsequent 1,3-dipolar cycloadditions of the azomethine ylide intermediates to homomultiple and heteromultiple bonds to give a variety of heterocycles are firmly established by several groups of workers.[4] When the aziridine ring is constrained in a bicyclic structure of medium size (five-or six-membered ring) at the 2,3 bond, disrotatory photochemical opening is allowed, but thermal conrotatory ring opening is not permitted by the geometry of the system. The latter reaction is therefore a disallowed process. In agreement with this prediction Huisgen reported[5] that the bicyclic aziridine **1**, while it undergoes facile photochemical disrotatory opening to species **2** which was subsequently trapped with dimethyl acetylenedicarboxylate to give **3** in 70% yield, was totally unreactive when heated to temperatures of even 180°.

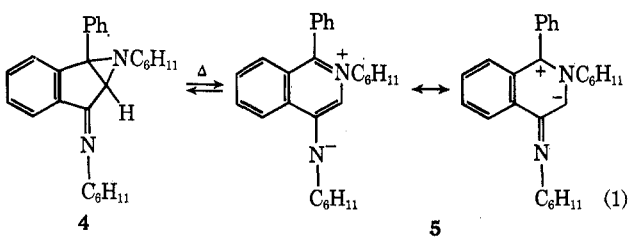


1 **2**

3

Oida and Ohki similarly recognized that in a bicyclic aziridine closely related to **1**, while photochemical disrotatory opening is allowed, thermal conrotatory ring opening is disallowed.[4j]

We report the thermally disallowed valence tautomerization of 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine **4** to the isoquinolinium imine **5** (see eq 1) and subsequent trapping of the latter as an azomethine ylide in a series of cycloadditions. The phenylindano[1,2-*b*]aziridine[6] is a white



4 **5** (1)

(1) (a) A preliminary report of this work has appeared previously: J. W. Lown and K. Matsumoto, *Chem. Commun.*, 692 (1970). (b) We are indebted to the National Research Council of Canada (Grant A2305) for financial aid. (c) National Research Council of Canada Postdoctoral Fellow, 1969–present.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 57.

(3) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

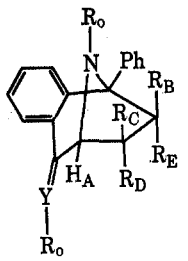
(4) (a) P. B. Woller and N. H. Cromwell, *J. Heterocycl. Chem.*, **5**, 579 (1968); (b) H. W. Heine and R. Peavy, *Tetrahedron Lett.*, 3123 (1965); (c) R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *ibid.*, 397 (1966); (d) A. Padwa and L. Hamilton, *ibid.*, 4363 (1965); (e) R. von Capeller, R. Griot, M. Haring, and T. Wagner-Jauregg, *Helv. Chim. Acta*, **40**, 1652 (1957); (f) H. W. Heine, A. B. Smith, and J. D. Bower, *J. Org. Chem.*, **33**, 1097 (1968); (g) H. W. Heine, R. E. Peavy, and A. J. Durbetaki, *ibid.*, **31**, 3924 (1966); (h) A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967); (i) A. Padwa and W. Eisenhardt, *Chem. Commun.*, 380 (1968); (j) S. Oida and E. Ohki, *Chem. Pharm. Bull.*, **16**, 764 (1968); (k) H. W. Heine and R. Henzel, *J. Org. Chem.*, **34**, 171 (1969); (l) J. W. Lown and J. P. Moser, *Chem. Commun.*, 247 (1970); (m) G. Dallas, J. W. Lown, and J. P. Moser, *ibid.*, 278 (1970); (n) J. W. Lown, J. P. Moser, and R. Westwood, *Can. J. Chem.*, **47**, 4335 (1969); (o) J. W. Lown, T. W. Maloney, and G. Dallas, *ibid.*, **48**, 584 (1970); (p) J. W. Lown, G. Dallas, and T. W. Maloney, *ibid.*, **47**, 3557 (1969); (q) J. W. Lown, R. K. Smalley, G. Dallas, and T. W. Maloney, *ibid.*, **48**, 89 (1970); (r) J. W. Lown, R. K. Smalley, G. Dallas, and T. W. Maloney, *ibid.*, **48**, 103 (1970); (s) J. W. Lown, R. Westwood, and J. P. Moser, *ibid.*, **48**, 1682 (1970).

(5) R. Huisgen and H. Mader, *Angew. Chem., Int. Ed. Engl.*, **8**, 604 (1969).

(6) N. H. Cromwell and M.C. McMaster, *J. Org. Chem.*, **32**, 2145 (1967).

TABLE I

ADDUCTS OF 1-ALKYL-6-(ALKYLIMINO)-1a-PHENYLINDANO[1,2-*b*]AZIRIDINES WITH OLEFINIC DIPOLAROPHILES[a]

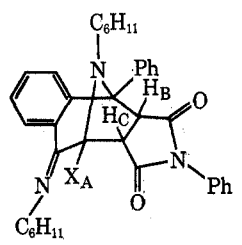


Adduct[b]	R_0	R_B	R_C	R_D	R_E	Mp, °C	Yield, %	Chemical shifts and coupling constants of methine protons[d]: δ in ppm from $(CH_3)_3Si$[e] H_A[g]	H_B	H_C	Hz[f]: J_{AC}	J_{BC}	J_{AD}
6	C_6H_{11}	H	H	CONPhCO		235–237	82	5.14, d (0.1 H)	4.32, d	3.87, t	9	9	
9a	C_6H_{11}	H	CO_2CH_3	H	CO_2CH_3	155–156	68	5.01, d (0.28 H)	4.30, d	3.37, q	1.8	7.3	
13	C_6H_{11}	H	H	$(CH_2)_4$		154–155	37	4.78, d (1 H)	2.6–3.2, m	2.1–2.6, m	8		
14	C_6H_{11}	H	H	CH—$(CH_2)_2$CH		174–175	39	4.66, d (0.57 H)	2.74, d	2.34, t	8	10	
15	C_6H_{11}	H	H	CHCH=CHCH		143–144	32	4.49, d	3.18, d	2.69, t	9	9	
19a	CH_3	H	H	CONPhCO		216–217	85	4.94, d	4.55, d	4.17, q	8.5	9.5	
19b	CH_3	H	H	$(CH_2)_4$		128–129	56	4.56, d	2.9–3.2, m	2.5–2.9, m	8		
20	C_6H_{11}	H	H	H	CN	206–207	45	4.73, q (0.1 H)	3.61, q	2.5, m	8	10	1.5
21a[c]	CH_3	H	H	H	CN	146–148	66	3.7–4.1, m	3.7–4.1, m	2.7–3.2, m	8.5	11	1.5
21b	C_6H_{11}	H	H	H	$CONH_2$	183	53	4.74, q	3.85, q	2.3–2.7, m	8	11	1.5
22[h]	C_6H_{11}	H	H	CH_3	CN	192–193	51	4.78, d (0.5 H)	3.87, d	2.5–3.0, m	8	11	

[a] Satisfactory analytical data (±0.4% for C, H, and N) and mass spectral molecular masses (±0.001) were reported for all compounds in table: Ed. [b] Y = N except as noted. [c] Y–R_0 = O. [d] All adducts showed absorption due to aromatic and vinyl protons in the range δ 6.0–8.4 with the appropriate integration and absorption in the range δ 0.5–2.7 due to C_6H_{11} with the cyclohexyl methine protons absorbing in the range δ 2.1–2.8 and 3.3–3.8. [e] H_D octet line positions for **20**, **21a**, and **21b** were 1.80, 1.94, and 1.85, respectively. [f] J_{BD} values for **20**, **21a**, and **21b** were 7 Hz. J_{CD} values for **20** and **21a** were 13 and 14 Hz, respectively. [g] Reduced in intensity to the value shown in parentheses in the bridgehead deuterated analog. [h] Contains a small amount of an isomer (<5%).

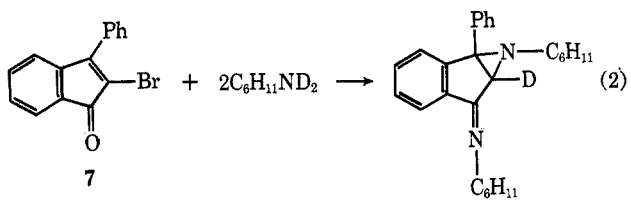
crystalline solid which is very sensitive to visible light, and, on exposure to daylight, adopts a red-purple color which fades in the dark. Solutions of **4** in toluene or xylene at about 135° assume an intense purple color which fades upon cooling or is bleached rapidly by sunlight. This purple species proved to be sensitive to oxygen, peroxides, halogens, acids, bases, and mercaptans, all of which added in trace quantities resulted in rapid bleaching of the color. The assignment of the purple species as the isoquinolinium imine **5** was supported by efficient trapping with a variety of dipolarophiles.

Heating of a degassed solution of **4** with an equimolar quantity of *N*-phenylmaleimide in toluene at 135° for 12 hr or refluxing in *p*-xylene under nitrogen afforded the crystalline adduct **6**, mp 235–237°, in 82% yield corresponding to 1,3-dipolar cycloaddition[7] across the azomethine ylide system (see Table I). Com-



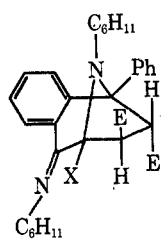
6a, X = H
b, X = D

pound **6** was assigned a configuration in which the *N*-phenylmaleimide moiety is endo with respect to the cyclohexylimino group on the basis of the nmr spectrum which showed 9-Hz coupling to the bridgehead proton, in agreement with a dihedral angle of approximately 20° predicted from an examination of molecular models and by comparison with other adducts **14**, **15**, **19a**, **20**, **21a**, **21b**, and **22** (see Figure 1A and Table I). The nmr assignments of the methine protons in **6** could be made unambiguously by examination of the analogous adduct **6a** obtained with specifically 2a-deuterated **8** prepared from the monobromo precursor **7** and cyclohexylamine-*N*-d_2[8] with 91% deuterium incorporation.



7 **8** (2)

A characteristic property of 1,3-dipolar cycloadditions is the stereospecificity of addition with respect to the dipolarophile.[7] However, reaction of **4** with an equimolar quantity of dimethyl fumarate or dimethyl maleate in degassed toluene at 135° for 48 hr afforded the identical adduct **9a**, mp 156–157°.



9a, X = H
b, X = D
E = $COOCH_3$

(7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

(8) D. B. Denney and M. A. Greenbaum, *J. Amer. Chem. Soc.*, **79**, 3701 (1957).

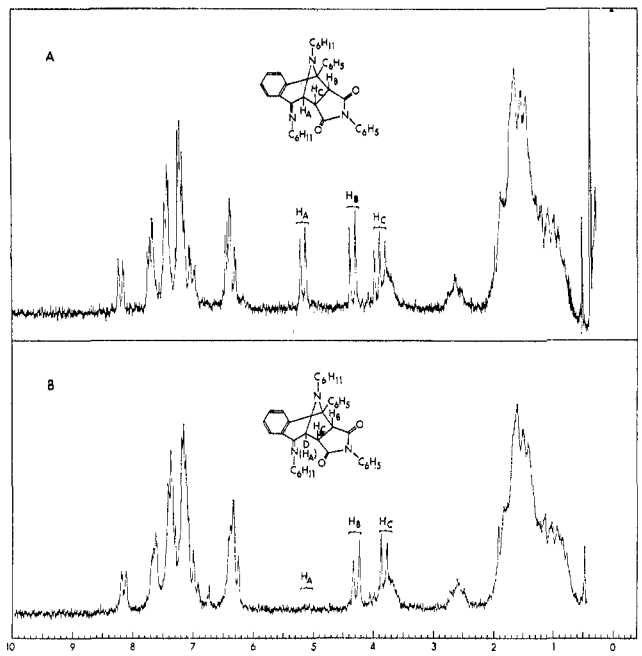


Figure 1.—Nuclear magnetic resonance spectrum at 100 MHz in $CDCl_3$ of (A) *N*-phenylamaleimide adduct of 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine, and (B) *N*-phenylamaleimide adduct of 1-cyclohexyl-6-(cyclohexylimino)-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine (91% deuterium).

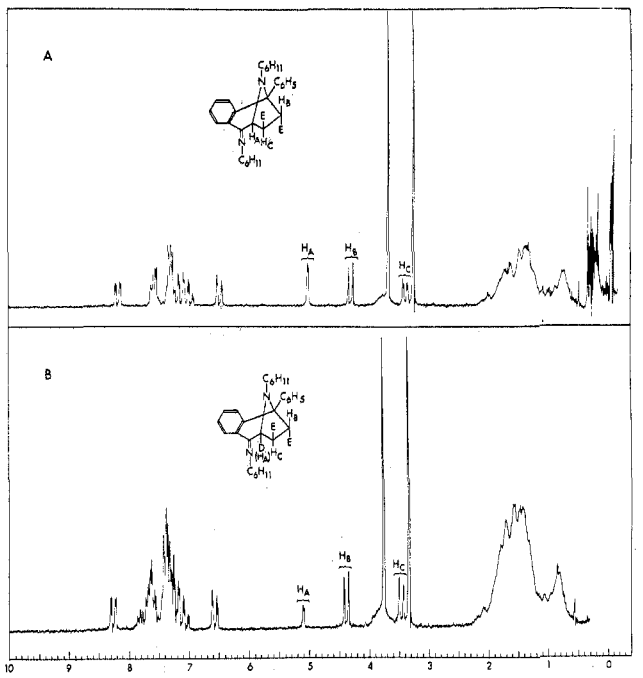
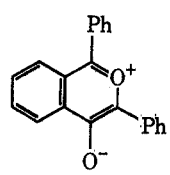


Figure 2.—Nuclear magnetic resonance spectrum at 100 MHz in $CDCl_3$ of (A) dimethyl maleate adduct of 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine, and (B) dimethyl maleate adduct of 1-cyclohexyl-6-(cyclohexylimino)-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine (91% deuterium); E = carbomethoxy group.

in 68 and 54% yields, respectively, corresponding in geometry to the addition of a fumarate moiety. Evidently the prolonged heating at 135° required to effect the disallowed ring opening of **4** results in isomerization of dimethyl maleate to dimethyl fumarate prior to cycloaddition.[9]

The orientation of the addition of the fumarate moiety in **9a** together with unambiguous assignment of the nmr methine line positions was possible by examination of the bridgehead deuterated analog **9b** (see Figures 2A and B). The diminution of the δ 5.01 doublet upon deuteration confirms the assignment of the bridgehead proton and its 1.8-Hz coupling to proton C confirms that the orientation of these protons is opposite to that which obtains in adduct **6**. The assignment of the 7.3-Hz splitting to a trans H_B–H_C coupling receives support by examination of adduct **20** described below.

Although the thermal valence tautomerization of **4** to **5** is formally a forbidden process, substantial driving force for this process is provided by the relief of ring strain[10] in **4** and the gain in resonance energy in **5**. This process is analogous to the observed reversible tautomerization of 2,3-diphenylindenone oxide to the red pyrylium 4-oxide **10** and of cyclopentadienone oxides to the red pyrylium oxides **11**.[11] Huisgen pointed



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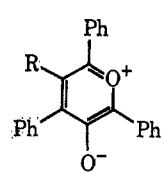
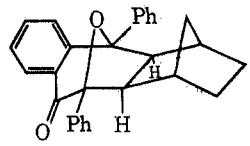


11

out[7] the carbonyl ylide nature of the pyrylium oxides **10** and **11** which readily react with dipolarophiles in 1,3-dipolar additions or dimerize readily. While an analogy may therefore be drawn between species **5** and **10** and **11**, significant differences in their properties may be noted.

The pyrylium oxide **10** forms an exo adduct **12** with norbornadiene, whereas **5** forms exclusively endo adducts. For example, **5** forms **6**, and **13**, which was obtained in 37% yield from cyclohexene. Compound



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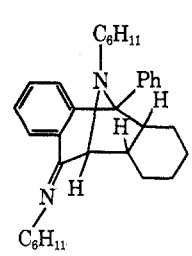

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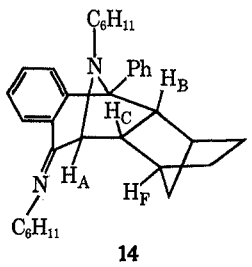
(9) Dimethyl maleate retains its configuration during the addition to 3-benzoyl-1-cyclohexyl-2-(2-thienyl)aziridine in refluxing benzene [J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **48**, 2215 (1970)], whereas addition of dimethyl maleate to 1,2,3-triphenylaziridine in refluxing toluene gave a fumarate adduct.[4g] Partial isomerization of dimethyl maleate occurs during the addition to 4-oxazolines to give 3-aroyl-4,5-dihydrofurans[4r] and Huisgen reported complete thermal isomerization of maleate in an attempt to observe stereospecific cycloaddition of a ketocarbene to maleate and fumarate: R. Huisgen, H. Konig, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).

(10) For example, although the analogy is not exact, D. R. Arnold and L. A. Karnishky [*J. Amer. Chem. Soc.*, **92**, 1404 (1970)] point out that the thermal bond homolysis of the central bond of bicyclopentane requires *ca.* 20 kcal mol^{-1} less energy than bond homolysis in dimethylcyclopropane: J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 22 (1960).

(11) (a) E. F. Ullman and J. E. Milks, *J. Amer. Chem. Soc.*, **84**, 1315 (1962); (b) E. F. Ullman, *ibid.*, **85**, 3529 (1963); (c) E. F. Ullman and J. E. Milks, *ibid.*, **86**, 3814 (1964); (d) E. F. Ullman and W. A. Henderson, *ibid.*, **86**, 5050 (1964); (e) J. M. Dunston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

14 was obtained by reaction of 4 with norbornene in 40% yield, and 15 was similarly obtained from



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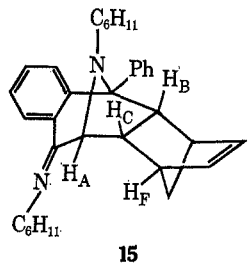

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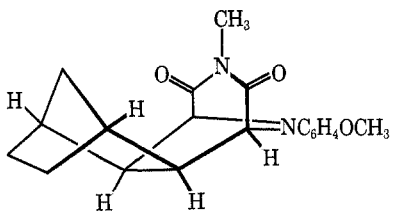
norbornadiene in 32% yield. The configuration of the adduct 13 was established by the 8-Hz coupling to the bridgehead proton by analogy with 6. Similarly adducts 14 and 15 were assigned structures endo with respect to the isoquinolinium moiety because of the magnitude of the coupling J_{AC} to be bridgehead proton (8 and 9 Hz, respectively) but exo structures with respect to the norbornene and norbornadiene moieties because $J_{CF} = 0$ Hz in agreement with assignments made on adducts 16 and 17 by Huisgen and his coworkers.[5] In accordance with this assign-



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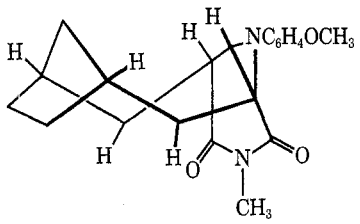
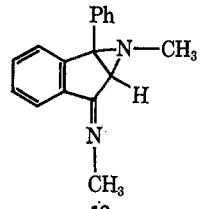


17

ment, it may be noted that norbornene and norbornadiene normally form exo Diels–Alder and 1,3-dipolar adducts.[12]

An additional difference in properties between 5 and 10 or 11 is that, whereas 4 could be recovered in good yield after pyrolysis in the absence of a dipolarophile (see later discussion), the unrecovered 2,3-diphenylindenone oxide in comparable experiments performed by Ullman and Milks[10c] proved to be a mixture of dimers. The *N*-cyclohexyl group in the isoquinolinium group of 5 probably exerts substantial steric hindrance during the 1,3-dipolar cycloaddition which directs a dipolarophile into the endo configuration and prevents dimerization of 5. Tetrasubstituted dipolarophiles such as tetracyanoethylene failed to react with 4. However, the fact that the smaller *N*-methyl substituent in 18 similarly results in the exclusive formation of endo adducts 19a and 19b suggests that other factors besides steric hindrance direct the mode

(12) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959).



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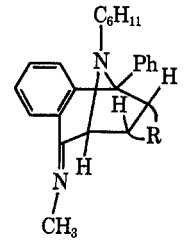
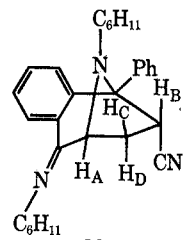


19a, R = C(=O)–N(Ph)–C(=O)–
b, R = $(CH_2)_4$

of addition of the dipolarophile. We examined unsymmetrical dipolarophiles to establish any possible orientation preference in the addition. Reaction of 4 with an excess of acrylonitrile afforded only one isolable adduct in 52% yield to which structure 20 could be



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assigned unambiguously by examination of the nmr spectrum together with critical double irradiation experiments (see Table II).

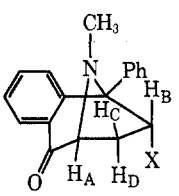
TABLE II

DOUBLE IRRADIATION EXPERIMENTS ON ADDUCTS OF INDANO[1,2-*b*]AZIRIDINE AT 100 MHz[a]

Adduct	Proton irradiated	Decoupling frequency (Hz)[b]	Lines collapsed: Original form	Lines collapsed: Final form	Measured coupling constant, Hz
14	H_A	466	t, 2.34, H_C	d	J_{AB} = 10
	H_A	466	d, 2.74, H_B	Unaffected	
20	H_C	266	q, 4.73, H_A	d	J_{AD} = 1.5
	H_C	266	q, 3.61, H_B	d	J_{BD} = 7
21a	H_D	206	q, 3.88, H_A	d	J_{AC} = 8.5
	H_D	206	q, 3.87, H_B	d	J_{CB} = 11
21b	H_A	470	m, 2.5, H_C	q	J_{BC} = 11
					J_{CD} = 14
	H_C	252	q, 4.74, H_A	d	J_{AD} = 1

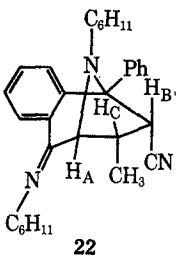
[a] Double irradiation experiments performed with Varian HA-100 nmr spectrometer. [b] From $(CH_3)_4Si$.

Similarly aziridine 18 reacted with acrylonitrile to give adduct 21a in which, however, the 6-methylimino group from 18 was eliminated by hydrolysis during the work-up procedure. Acrylamide reacted with 4 to give adduct 21b in 53% yield, the structure of which was proven by deuterium labeling and spin decoupling.



21a, X = CN
b, X = $CONH_2$

The operation of strong directional effects in the approach of the dipolarophile to **5** is demonstrated by the reaction of **4** with a cis–trans mixture of crotonitrile. The adduct obtained proved to be that formed from *cis*-crotonitrile exclusively, *i.e.*, **22** in which both larger groups may be accomodated remote from the bridge-*N*-cyclohexyl group. The stereochemical assignment of **22** is confirmed by observation of J_{AC} = 8 Hz and J_{BC} = 11 Hz both typical of cis vicinal coupling in a pyrrolidine structure.[4g] The appearance of H_B as a simple

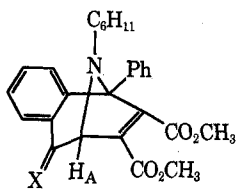


22

11-Hz doublet and its line position at δ 3.87 supports **22** and excludes the structure in which the dipolarophile is added in the alternative orientation.

The structure of the minor isomer produced in this reaction could not be assigned with confidence owing to the relatively low intensity of its nmr spectrum.

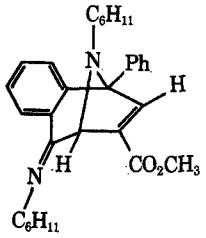
Reaction of **4** with dimethyl acetylenedicarboxylate in toluene gave **23a** in 70% yield. The nmr spectrum of **23a** consisted of a closely similar pair of isomers showing two distinct singlets for the bridgehead proton



23a, X = NC_6H_{11}
b, X = O

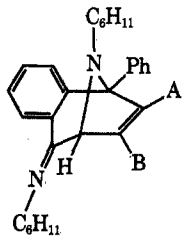
(*both* of which disappear in the adduct formed from **8** and dimethyl acetylenedicarboxylate) and two sets of signals for the ester methyl groups in the same proportion. This we attribute to the existence of syn and anti stereoisomerism about the 6-cyclohexylimino group, since mild acid hydrolysis of the mixture of isomers **23a** gave a single keto compound **23b**. The nmr spectrum of **23b** showed one sharp singlet for the bridgehead proton at δ 4.80. This phenomenon of syn–anti stereoisomerism, which occurred in the case of acetylenic adducts of **4**, was not encountered in adducts of olefinic dipolarophiles. Presumably the operation of directional effects which place larger groups endo to the cyclohexylimino group in **6**, **13**, **14**, **15**, **19a**, **19b**, and **22** preclude the existence of a syn configuration analogous to **23a**.

Similarly, reaction of methyl propiolate with **4** gave a mixture of stereoisomeric adducts in 63% yield, the major portion of which (>90%) consisted of structure **24** which like **23** exists as a syn–anti stereoisomeric mixture. Both of these stereoisomers showed doublets from AB quartets (J_{AB} = 2.7 Hz) for the bridgehead protons at δ 4.46 and 5.08, respectively, which were confirmed by deuteration to the extent of 90%. The intensity of these signals was 10% of one proton in a sample separately prepared from **8**. The magnitude of this vicinal coupling corresponds with that reported for the model compound norbornene in which J_{AB} = 2.2–3.3 Hz.[13]



24

Methyl phenyl propiolate reacted with **4** to give a mixture of isomers **25a** and **25b**. In this instance, as in the case of the diphenylacetylene adduct **26**, distinct nmr signals due to each syn and anti isomer were not observed.



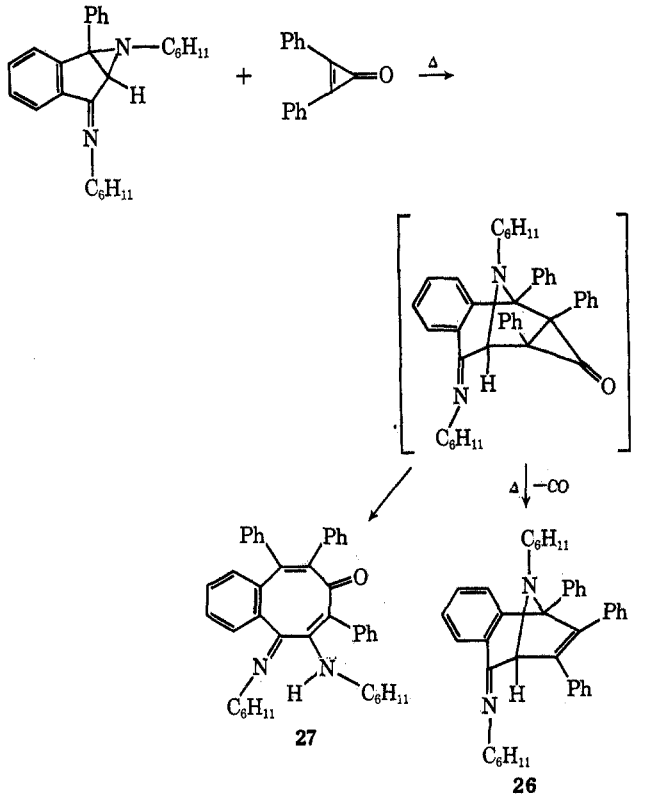
25a, A = CO_2CH_3; B = Ph
b, A = Ph; B = CO_2CH_3

The dipolarophilic capacity of the carbon–carbon double bond in diphenylcyclopropenone is considerable,[4o] and in many of its 1,3-dipolar cycloadditions to 3-aroylaziridines it forms pyrrolines by expulsion of carbon monoxide and thus behaves as a more reactive form of diphenylacetylene. Reaction of diphenylcyclopropenone[14] with **4** in toluene at 135° gave two products formulated as **26** and **27**. The former was identical with that obtained from diphenylacetylene and its formation is rationalized in Scheme I. The second product **27** proved to be a 1:1 adduct (*i.e.*, carbon monoxide was not eliminated), and the spectral data were consistent with structure **27**: ir 3400 (NH), 1624 (diconjugated C=O), 1600 cm^{-1} (C=C and C=N); nmr 3.30 (broad singlet exchangeable by deuterium oxide NH). The latter product resembles those obtained by reaction of diphenylcyclopropenone and enamines by Ciabattoni and Berchtold.[15]

Nature of the Ring-Opened Species.—Rapid determination of the visible absorption spectrum of the colored species obtained by heating **4** to 135° in xylene showed an intense absorption maximum at 505 mμ with shoulders at 534 and 570 mμ. The ring opening depicted by eq 1 is demonstrably reversible as shown by parallel experiments carried out in the presence and in the absence of *N*-phenylmaleimide, a powerful dipolarophile. The fraction of **5** consumed in the presence of a trapping agent (>80%) exceeded the fraction used up in its absence (39%), and hence the untrapped isoquinolinium imine **5** must be thermally reconverted back to the indanoaziridine **4**. A similar argument

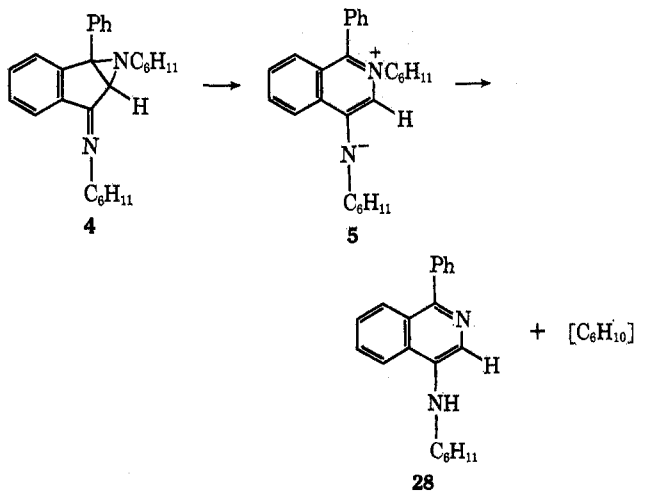
(13) P. Laszlo, *Science*, 58 (1963).
(14) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).
(15) J. Ciabattoni and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966).

SCHEME I



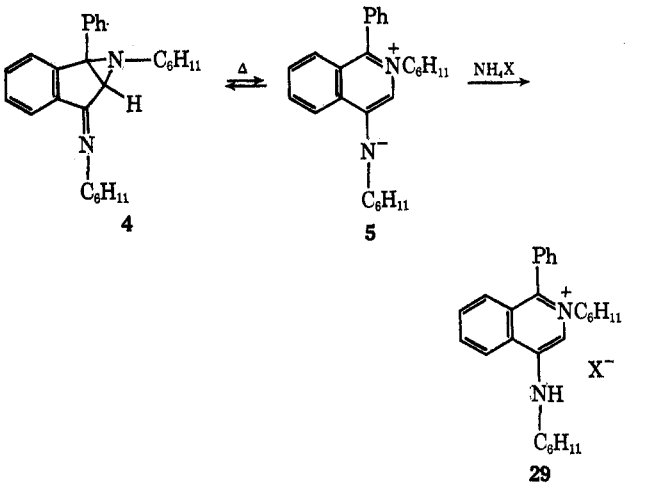
was employed by Ullman and Milks to demonstrate the reversibility of the valence tautomerism of 2,3-diphenylindenone oxide.[10c]

Prolonged pyrolysis of **4** in the absence of dipolarophiles or in the presence of very unreactive dipolarophiles such as cyclohexanone or benzonitrile resulted in the formation of **28**.

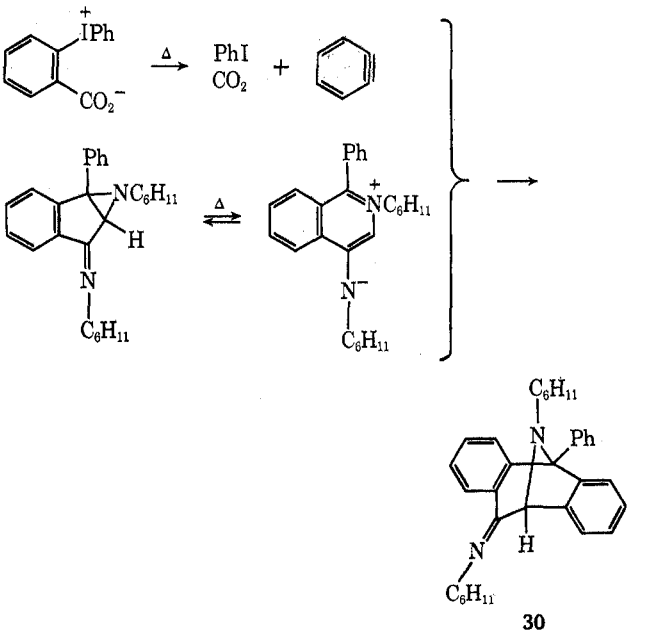


The elimination of cyclohexene from **5** to form the stable aromatic product **28** finds a parallel in the elimination of hydrocarbons from intermediate 4-oxazolines to form aromatic oxazoles reported by Padwa and Hamilton.[16]

The observed thermal opening of **4** to **5** complements the recently described[17] allowed solvolytic disrotatory opening of the *N*-chloroindano[1,2-*b*]aziridine to a nitrenium ion, which is an electrocyclic process with the same orbital symmetry control as a cyclopropyl to allyl cation rearrangement.[18] The intermediate nitrenium ion is converted to isoquinoline by loss of a proton. A parallel is provided in the present work; when the ylide **5** abstracts a proton from added ammonium halide, it is converted into the more stable salt **29**[19] which is the conjugate acid of the ylide.



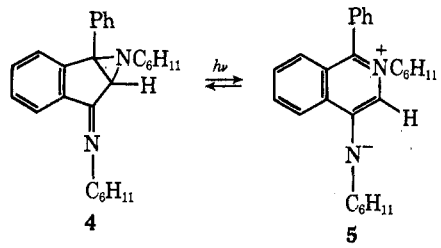
Some measure of the resonance stabilization available to **5** and its consequent relatively long lifetime is provided by its successful trapping with benzyne. Heating a mixture of **4** with the benzyne precursor diphenyliodonium-2-carboxylate[20] in mesitylene gave the adduct **30**. This indicates qualitatively that **5** is relatively stable and long-lived, since repeated attempts to trap the azomethine ylide from 1,2,3-triphenylaziridine with benzyne proved unsuccessful. Another factor contributing to the relative stability of species **5** is that



(16) A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 1861 (1967).
(17) D. C. Horwell and C. W. Rees, *Chem. Commun.*, 1428 (1969).
(18) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanism," Wiley, New York, N. Y., 1965, p 44; 1966, p 37; 1967, p 50; 1968, p 49.
(19) This reaction of **5** results in a sensitivity of the azomethine ylide to dipolarophiles possessing mobile protons; *e.g.*, while *N*-phenylmaleimide gave **6** in 82% yield, the apparently closely related dipolarophile maleimide gave in addition to only a small amount of adduct a complex mixture of unidentified products.
(20) F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

ring closure of the azomethine ylide by a symmetry-allowed conrotatory process[21] would result in a trans-fused ring which is clearly not permitted by the geometry of the system.

Photochemical Valence Tautomerization of the Indano[1,2-*b*]aziridine.—Whilst the geometry of **4** should not allow conrotatory opening to species **5** under thermal conditions, the corollary is that photochemical disrotatory cleavage should be facile. Photolysis of dilute solutions of **4** in dioxane or ether at 0° in a quartz reaction vessel produced an immediate deep red color, the absorption spectrum of which corresponded closely with that of the colored species produced thermally. The red color is discharged rapidly upon exposure to visible light and the infrared spectrum of the bleached solution was superimposable with that of **4**. Photolysis of solutions of **4** in dichloroethylene resulted in photolytic abstraction of hydrogen chloride from the sol-



4 **5**

vent and production of the yellow salt **29** (X = Cl) in good yield.

This compound was identical in properties with that produced thermally and thus represents the photochemical stabilization of **5** by proton abstraction.

A control experiment involving irradiation of solutions of **4** in the epr cavity of a Varian instrument generated the deep red color but produced no evidence of a diradical species even at low temperatures. We conclude that **4** undergoes facile reversible photochemical disrotatory cleavage to an azomethine ylide identical with that produced thermally.

Repeated attempts to trap this species generated photolytically at low temperature with dipolarophiles such as *N*-phenylmaleimide proved unsuccessful. However, this result is not unexpected since, while 3-aroylaziridines readily give 1,3-dipolar cycloaddition adducts in good yield with a variety of dipolarophiles in refluxing benzene, Padwa and Hamilton were unable to trap the analogous azomethine ylides produced photolytically.[4h] Similarly, in Huisgen's classic demonstration of the thermal conrotatory and photolytic disrotatory opening of aziridine derivatives,[3] the yields of 1,3-dipolar adducts obtained thermally were superior to those obtained photochemically. In the recently announced photolytic disrotatory cleavage of oxiranes to carbonyl ylides[22] and thermal cleavage to similar species,[21d] 1,3-dipolar addition adducts were formed thermally but not under photolytic conditions.

Experimental Section

General.—Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. Nuclear magnetic resonance spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10–15% (w/v) solutions in $CDCl_3$, with tetramethylsilane as a standard. Line positions are reported in parts per million from the reference. Absorption spectra were recorded in "spectro" grade solvents on a Beckman DB recording spectrophotometer. Mass spectra were determined on an Associated Electrical Industries MS-9 double-focusing high-resolution mass spectrometer. The ionization energy, in general, was 70 eV. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15,000. Kieselgel DF-5 (Camag, Switzerland) and Eastman Kodak precoated sheets were used for thin layer chromatography. Microanalyses were carried out by Dr. C. Daesslé, Organic Microanalysis Ltd., Montreal, Quebec, and by Mrs. D. Mahlow of this department.

1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine and 1-Methyl-6-(methylimino)-1a-phenylindano[1,2-*b*]aziridine.—These compounds were prepared according to the method of Cromwell.[6] The cyclohexylindanoaziridine had mp 158–159° (lit.[6] 159–160°). The methylindanoaziridine had mp 98–99° (lit.[6] 98–99°).

Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Olefinic Dipolarophiles.—*N*-Phenylmaleimide, dimethyl maleate, dimethyl fumarate, acrylonitrile, acrylamide, norbornene, norbornadiene, and cyclohexene were successfully employed as dipolarophiles. The reaction procedure is exemplified by the following three reactions.

Reaction of 1-Cyclohexylimino-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with *N*-Phenylmaleimide.—A solution of 0.770 g (2 mmol) of the indano[1,2-*b*]aziridine **4** and 0.346 g (2 mmol) of *N*-phenylmaleimide in 30 ml of *p*-xylene was heated under reflux under nitrogen for 12 hr. Removal of the solvent *in vacuo* gave a red oil, trituration of which with hexane afforded adduct **6a** as a slightly purple solid, 0.925 g (82%), purified by recrystallization from ethyl acetate–hexane: mp 235–237°; ir ($CHCl_3$) 1649 (C=N), 1713, 1775 cm^{-1} (C=O); nmr δ_{TMS} ($CDCl_3$) 0.5–2.2 (m, 20, C_6H_{11}), 2.2–2.9 (m, 1, CHN), 3.5–4.1 (m, 1, C=NCH), 3.87 (t, 1, J_{AC} = 9 Hz, H_C), 4.32 (d, 1, J_{BC} = 9 Hz, H_B), 5.14 (d, 1, J_{AC} = 9 Hz H_A), 6.0–8.3 (m, 14, aromatic protons) (see Figure 1A); uv_{max} (95% EtOH) 247 mμ (log ε 4.12), 290 (sh, 3.06), 304 (sh, 2.62); mass spectrum (70 eV) 557.3042 (calcd for $C_{37}H_{39}N_2O_2$, 557.3042).

Anal. Calcd for $C_{37}H_{39}N_2O_2$: C, 79.68; H, 7.05; N, 7.54. Found: C, 79.86; H, 6.86; N, 7.53.

Reaction of 1-Cyclohexylimino-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Dimethyl Fumarate.—A deoxygenated solution of 1.15 g (3 mmol) of the indano[1,2-*b*]aziridine **4** and 0.432 g (3 mmol) of dimethyl fumarate in 30 ml of toluene was heated to 135–145° in a sealed vessel for 48 hr. Removal of the solvent *in vacuo* gave **9a** as a slightly purple solid, 1.074 g (68%): mp 156–157° (ether-pentane); ir ($CHCl_3$) 1642 (C=N), 1731 cm^{-1} (C=O); nmr δ_{TMS} ($CDCl_3$) 0.5–2.2 (m, 21, C_6H_{11}), 3.23 (s, 3, CO_2CH_3), 3.37 (q, 1, J_{BC} = 7.3 Hz, J_{AC} = 1.8 Hz, H_C), 3.65 (s, 3, CO_2CH_3), 4.30 (d, 1, J_{BC} = 7.3 Hz, H_B), 3.5–3.9 (m, 1, C=NCH), 5.01 (d, 1, J_{AC} = 1.8 Hz, H_A), 6.4–8.3 (m, 9, aromatic protons) (see Figure 2A); uv_{max} (95% EtOH) 242 mμ (log ε 4.16), 278 (sh, 3.14); mass spectrum (70 eV) 528.2995 (calcd for $C_{33}H_{40}N_2O_4$, 528.2988).

Anal. Calcd for $C_{33}H_{40}N_2O_4$: C, 74.97; H, 7.63; N, 5.30. Found: C, 74.77; H, 7.49; N, 5.55.

Reaction of 1-Cyclohexylimino-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Dimethyl Maleate.—A deoxygenated solution of 1.15 g (3 mmol) of the indano[1,2-*b*]aziridine **4** and 0.432 g (3 mmol) of dimethyl maleate in 30 ml of toluene was heated to 135–145° in a sealed vessel for 48 hr. Removal of the solvent *in vacuo* gave an adduct **9a** identical in all respects with that obtained above from dimethyl fumarate, 0.857 g (54%), mp 156–157° (ether-pentane).

Reactions of 1-Cyclohexylimino-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Other Olefinic Dipolarophiles.—Similar reactions were carried out with 3 mmol of either indano[1,2-*b*]aziridine and 10 ml each of acrylonitrile, crotonitrile, norbornadiene, or cyclohexene or 10 equiv of norbornene in 30 ml of toluene for reflux periods of up to 48 hr. Analytical and spectroscopic data on the adducts thus obtained are summarized in Tables I and II. Critical double irradiation experiments on selected adducts used to determine coupling constants and to assign structures are reported in Table II.

(21) (a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (b) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (c) B. G. Gill, *Quart. Rev., Chem. Soc.*, **22**, 338 (1968); (d) D. R. Arnold and L. A. Karnishky, *J. Amer. Chem. Soc.*, **92**, 1404 (1970).

(22) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *ibid.*, **92**, 1402 (1970).

6-Cyclohexylimino-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine (9). A. 2-Bromo-3-phenylindenone[6] (8).—2-Bromo-3-phenylindenone was prepared by the following improved procedure. A mixture of 33.6 g (0.1 mol) of 2,3-dibromo-3-phenylindenone[23] and 10.8 g (0.11 mol) of potassium acetate in 700 ml of 95% ethanol was refluxed for 6 hr. Concentration of the solution *in vacuo* gave 2-bromo-3-phenylindenone (**7**) as orange crystals from ethanol, 24.8 g (97%), mp 112–113° (lit.[23] mp 112–113°).

B. 6-Cyclohexylimino-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine.—To a slurry of 25.5 g (0.1 mol) of 2-bromo-3-phenylindenone in 200 ml of dry benzene, a solution of 40 g (0.4 mol) of cyclohexylamine-N-d_2[8] was added dropwise with stirring, and stirring was continued 3 days in the dark. Removal of the solvent gave a brown solid, trituration of which with 95% ethanol gave pure aziridine **8** as a white solid, 30.8 g (80%): mp 159–160°; nmr δ_{TMS}($CDCl_3$) 0.5–2.2 (m, 21, C_6H_{11}), 3.23 (s, 0.09, bridgehead proton), 3.4–4.0 (m, 1, C=NCH), 7.0–8.0 (m, 9, aromatic protons). An average of several integrations confirmed 91% deuterium incorporation at the bridgehead position.

Reaction of 6-Cyclohexylimino-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine with Olefinic Dipolarophiles.—In order to elucidate the stereochemistry of some of the adducts obtained by reaction of indano[1,2-*b*]aziridines **4** with olefinic dipolarophiles, additions of the 2a-deuterated analog were carried out as exemplified by the reaction with N-phenylmaleimide. The results of other similar experiments are summarized in Table I.

Reaction of 6-Cyclohexylimino-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine with N-Phenylmaleimide.—A deoxygenated solution of 1.16 (3 mmol) of 6-cyclohexylimino-2a-deuterio-1a-phenylindano[1,2-*b*]aziridine (**8**) and 0.519 g (3 mmol) of N-phenylmaleimide in 30 ml of toluene was heated at 135–145° for 24 hr. Evaporation of the solvent gave a purple oil, trituration of which with hexane gave a pale purple solid **6b**, 1.322 g (79%): mp 236–237° (ethyl acetate–hexane); nmr δ_{TMS}($CDCl_3$) 0.5–2.2 (m, 20, C_6H_{11}), 2.2–2.9 (m, 1, CHN), 3.5–4.1 (m, 1, C=NCH), 3.87 (d, 1, J_{AC} = 9 Hz, H_C), 4.32 (d, 1, J_{BC} = 9 Hz, H_B), 5.14 (d, 0.1, H_A), 6.0–8.3 (m, 14 aromatic protons). An average of several integrations confirmed 90% deuterium incorporation at the bridgehead position.

Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Acetylenic Dipolarophiles.—Dimethyl acetylenedicarboxylate, methyl propiolate, diphenylacetylene, methyl phenylpropiolate, diphenylcyclopropenone, and benzyne were successfully employed as dipolarophiles. The reaction procedure and structure proof of the adducts for the first three dipolarophiles was similar to that described in detail for typical olefinic dipolarophile additions. The reactions involving the latter three acetylenic dipolarophiles are discussed in detail.

Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Methyl Phenylpropiolate.—A deoxygenated solution of 1.15 g (3 mmol) of the indano[1,2-*b*]aziridine **4** and 0.480 g (3 mmol) of methyl phenylpropiolate in 30 ml of toluene was heated to 135–145° for 40 hr. Evaporation of the solvent gave a purple oil which was subjected to chromatography on alumina. Elution with benzene gave one main fraction. Removal of the solvent *in vacuo* and trituration of the residual solid with hexane afforded adducts **25a** and **25b**, 0.914 g (56%): mp 172–173° (ether–hexane); ir ($CHCl_3$) 1638 (C=N), 1701 cm^{-1} (C=O); nmr δ_{TMS} ($CDCl_3$) 0.3–2.5 (m, 21, C_6H_{11}), 3.52 and 3.58 (s, 3 each, CO_2CH_3), 3.7–4.4 (m, 1, =NCH), 5.53 and 5.57 (s, 1, bridgehead proton; line position confirmed by deuteration to the extent of 71%), 6.8–8.4 (m, 14, aromatic protons); uv_{max} (95% EtOH) 248 mμ (log ϵ 4.34), 236 (sh, 4.30); mass spectrum (70 eV) 544.3084 (calcd for $C_{37}H_{40}N_2O_2$, 544.3090).

Anal. Calcd for $C_{37}H_{40}N_2O_2$: C, 81.55, H, 7.40, N, 5.14. Found: C, 81.12; H, 7.31; N, 5.19.

From the nmr spectrum it appears that two orientational isomers are present; however, repeated attempts at chromatographic separation were unsuccessful.

Reaction of 1-cyclohexyl-6-cyclohexylimino-1a-phenylindano[1,2-*b*]aziridine with (A) dimethyl acetylenedicarboxylate similarly gave adduct **23a** (71%): mp 68–70°; ir ($CHCl_3$) 1637 (C=N), 1724 cm^{-1} (ester C=O); nmr δ_{TMS} ($CDCl_3$) 0.3–2.5 (m, 21, C_6H_{11}), 3.5–4.2 (m, 1, C=NCH), 3.57, 3.78 (s, 3 each, CO_2CH_3), 4.9 (s, 0.4), 5.55 (s, 0.6, bridgehead proton), 6.8–8.3 (m, 9, aromatic protons).

B. Methyl propiolate similarly gave adduct **24** (61%): mp 73°; ir 1635 (C=N), 1716 cm^{-1} (ester C=O); nmr δ_{TMS} ($CDCl_3$) 0.3–2.4 (m, 21, C_6H_{11}), 3.3–3.7 (m, 1, C=NCH), 3.45, 3.50 (s, 3, CO_2CH_3), 4.46 (d, 0.5, J = 2.8 Hz), 5.08 (d, 0.5, J = 2.5 Hz, bridgehead proton), 6.8–8.3 (m, 10, aromatic protons).

Acid Hydrolysis of Adduct of 1-Cyclohexyl-6-cyclohexylimino-1a-phenylindano[1,2-*b*]aziridine with Dimethyl Acetylenedicarboxylate.—To a stirred solution of 0.526 g (1 mmol) of adduct **23a** in 20 ml of methanol was added 20 ml of 2 N hydrochloric acid. Stirring was continued for 5 hr at room temperature, the methanol was evaporated, and the residue was extracted with chloroform. Evaporation of the solvent from the dried ($MgSO_4$) extract gave a yellow solid **23b** which purified by recrystallization from chloroform–hexane, 0.307 g (69%): mp 134–135; ir ν_{max} ($CHCl_3$) 1640 (C=O), 1720 cm^{-1} (ester C=O); nmr δ_{TMS} ($CDCl_3$) 0.5–2.2 (m, 11, C_6H_{11}), 3.72 (s, 6, CO_2CH_3), 4.80 (3, 1, bridgehead proton), 6.7–8.0 (m, 9, aromatic protons); mass spectrum (70 ev) 445.1892 (calcd for $C_{27}H_{27}NO_5$, 445.1889).

Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Diphenylcyclopropenone.—A deoxygenated solution of 2.30 g (6 mmol) of the indano[1,2-*b*]aziridine **4** and 1.236 g (6 mmol) of diphenylcyclopropenone in 60 ml of toluene was heated for 48 hr at 135–145°. Removal of the solvent gave a dark red oil, trituration of which with 95% ethanol gave initially crude **27** as a yellow solid, 1.469 g (42%), purified by recrystallization from 95% ethanol: mp 223–224°; ir ($CHCl_3$) 1624 (C=O), 1618, 1595 cm^{-1} (C=N); nmr δ_{TMS} ($CDCl_3$) 0.3–2.5 (m, 21, C_6H_{11}), 3.28 (s, 1, exchangeable with D_2O, NH), 3.3–4.0 (m, 1, C=NCH), 6.7–7.7 (m, 19, aromatic protons); uv_{max} (95% EtOH) 250 mμ (log ϵ 4.22), 295 (3.79), 414 (3.97); mass spectrum (70 eV) 590.3297 (calcd for $C_{42}H_{42}N_2O$, 590.3297).

Anal. Calcd for $C_{42}H_{42}N_2O$: C, 85.38, H, 7.17, N, 4.74. Found: C, 84.95; H, 6.71; N, 4.98.

The filtrate obtained from the isolation of **27** was subjected to chromatography on alumina using benzene as eluent which gave adduct **26** as a colorless solid, 0.762 g (23%): mp 169–170° (95% ethanol); ir ($CHCl_3$) 1634 cm^{-1} (C=N); nmr δ_{TMS} ($CDCl_3$) 0.5–2.5 (m, 21, C_6H_{11}), 3.2–3.7 (m, 1, C=NCH), 5.62 (s, 1, bridgehead proton; line position confirmed by deuteration to the extent of 50%), 6.8–8.5 (m, 19, aromatic protons); uv_{max} (95% EtOH) 224 mμ (log ϵ 3.81), 257 (ϵ 3.63); mass spectrum (70 eV) 562.3340 (calcd for $C_{41}H_{42}N_2$, 562.3348).

Anal. Calcd for $C_{41}H_{42}N$: C, 87.50; H, 7.53; N, 4.98. Found: C, 87.45; H, 7.42; N, 5.07.

This compound was identical in all respects with that obtained directly by reaction of **4** with diphenylacetylene.

Reaction of 1-Cyclohexyl-6-cyclohexylimino-1a-phenylindano[1,2-*b*]aziridine with Diphenyliodonium-2-carboxylate.—A solution of 1.15 g (3 mmol) of the indano[1,2-*b*]aziridine **4** and 1.94 g (6 mmol) of diphenyliodonium-2-carboxylate[20] in 50 ml of 1,2,3-trimethylbenzene was heated under reflux for 10 hr under nitrogen. Removal of the solvent *in vacuo* gave a dark red oil which was subjected to chromatography on alumina. Initial elution with pentane removed aromatic by-products, while the main fraction was obtained by elution with benzene. Evaporation of the solvent *in vacuo* and several recrystallizations of the residue from 95% ethanol afforded adduct **30** as a pale yellow solid, 0.258 g (19%): mp 83–86° (95% ethanol); ir ($CHCl_3$) 1635 cm^{-1} (C=N); nmr δ_{TMS} ($CDCl_3$) 0.5–2.5 (m, 21, C_6H_{11}), 3.2–3.7 (m, 1, C=NCH), 5.65 (s, 1, bridgehead proton), 6.5–8.2 (m, 13, aromatic protons); uv_{max} (95% EtOH) 258 mμ (log ϵ 3.51), 226 (3.94); mass spectrum (70 eV) 460.2883 (calcd for $C_{33}H_{36}N_2$, 460.2878).

Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Dipolarophiles of Low Reactivity and in the Absence of Dipolarophiles.—A deoxygenated solution of 1.15 g (3 mmol) of the indano[1,2-*b*]aziridine **4** and 15 ml of cyclohexanone in 15 ml of toluene was heated to 135–145° for 48 hr. Removal of the solvent *in vacuo* gave a dark purple oil which was subjected to chromatography on alumina. Elution with benzene gave an oil from the main fraction, trituration of which gave **28** as a yellow solid, 0.346 g (38%): mp 123–124°; ir ($CHCl_3$) 3432 (NH), 1577 cm^{-1} (C=N); nmr δ_{TMS} ($CDCl_3$) 0.5–2.5 (m, 10, C_6H_{11}), 3.2–3.8 (m, 1, CHN), 4.10 (s, 1, exchangeable with D_2O NH), 7.2–8.3 (m, 10, aromatic protons); uv_{max} (95% EtOH) 262 mμ (log ϵ 4.06), 340 (sh, 3.91), 363 (4.03); mass spectrum (70 eV) 302.1787 (calcd for $C_{21}H_{22}N_2$, 302.1783).

Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.34; N, 9.27. Found: C, 83.19; H, 7.27; N, 9.14.

The identical compound was obtained by similar reaction of **4** with benzonitrile and vinylene carbonate in 19 and 23% yields,

(23) R. Weisz and S. Luft, *Monash. Chem.*, **48**, 338 (1927).

respectively. No unreacted aziridine could be detected after these prolonged reactions at high temperature.

Reversibility of the Thermal Valence Isomerization of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine. A. Reaction in the Absence of Dipolarophile.—A deoxygenated solution of 1.15 g (3 mmol) of **4** in 30 ml of toluene was heated to 135–145° for 24 hr giving a deep red color. Evaporation of the solvent and trituration of the residue with ethanol gave recovered indano[1,2-b]aziridine **4** as a slightly yellow solid, mp 158–159°, 0.702 g (61% recovery). Evaporation of the ethanol mother liquor afforded 0.068 g (19%) of **28**, 123–124°.

B. Parallel Reaction in the Presence of a Dipolarophile.—A similar experiment was performed with 1.5 g (3 mmol) of **4** and 0.519 g (3 mmol) of *N*-phenylmaleimide under exactly comparable conditions and resulted in the isolation of adduct **6** (see above), 1.34 g (80%), mp 235–236°, but no aziridine **4** could be recovered.

Reversibility of Photochemical Valence Isomerization of 1-Cyclohexyl-6-(6-cyclohexylimino)-1a-phenylindano[1,2-b]aziridine—A solution of 1.063 g (2.8 mmol) of the indano[1,2-b]aziridine **4** in 100 ml of tetrahydrofuran was irradiated under nitrogen at 0 to −10° in a quartz cell using a 450-W Hanovia high-pressure lamp for 8 hr. A deep red solution was obtained[24] and when exposed to visible light the color rapidly faded to a pale yellow resulting in a virtually complete restoration of the infrared absorption spectrum of the original compound **4**.

Photochemical Reaction between 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine and Cyclohexylamine Hydrobromide.—A mixture of 1.15 g (3 mmol) of the indano[1,2-b]aziridine **4** and 1.08 g (6 mmol) of cyclohexylamine hydrobromide in 150 ml of ether and 20 ml of methanol was irradiated for 8 hr under nitrogen with a 450-W high-pressure Hanovia lamp in a quartz reaction vessel. The resulting yellow solid **29** was collected and recrystallized from ether–methanol, 0.527 g (38%): mp 298–299°; ir ($CHCl_3$) 1617 (C=N), 3230 cm^{-1} (NH); nmr δ_{TMS} ($CDCl_3$) 0.6–2.4 (m, 20, C_6H_{11}), 3.0–3.6 (m, 1, CHNHC=), 3.9–4.5 (m, 1, $=N^+CH$), 6.8–8.1 (m, 9, aromatic protons), 8.51 (d, 1, D_2O exchangeable NH), 9.65 (d, 1, J = 7 Hz, aromatic protons); uv_{max} (95% EtOH–HBr) 393 mμ (log ε 4.12), 335 (3.77), 324 (sh, 3.72), 288 (3.86), 279 (3.89); mass spectrum (70 eV) 384.

Anal. Calcd for $C_{27}H_{33}N_2Br$: N, 6.02. Found: N, 5.56.

The identical compound was obtained by heating the indano[1,2-b]aziridine with cyclohexylamine hydrobromide or ammonium bromide in toluene.

Photochemical Reaction between 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine and *cis*-1,2-Dichloromethylene.—A mixture of 1.15 g (3 mmol) of the indano[1,2-b]aziridine **4** and 20 ml of *cis*-1,2-dichloroethylene in 100 ml of absolute ether was irradiated under nitrogen at 0 to 10° in a quartz reaction vessel for 8 hr. The resulting yellow solid was collected and purified by recrystallization from methanol–ether, 1.08 g (86%): mp 283–285°; ir ($CHCl_3$) 1618 (C=N), 3220 cm^{-1} (NH); nmr δ_{TMS} ($CDCl_3$) 0.7–2.5 (m, 20, C_6H_{11}), 3.3–3.7 (m, 1, =CNHCH), 4.1–4.5 (m, 1, $=^+NCH$), 7.1–8.2 (m, 9, aromatic protons), 8.54 (d, 1, D_2O exchangeable, NH), 8.68 (d, 1, J = Hz, aromatic proton); uv_{max} (95% EtOH) 222 mμ (log ε 4.59), 278 (3.66), 288 (3.64), 324 (sh, 3.47), 334 (3.55), 393 (3.99); mass spectrum (70 eV) 384.

Anal. Calcd for $C_{27}H_{33}N_2Cl$: N, 6.66. Found: N, 6.55.

The identical compound was obtained by heating the indano[1,2-b]aziridine with ammonium chloride in toluene.

Registry No.—**6a**, 27409-74-1; **6b**, 28443-72-3; **8**, 28443-73-4; **9a**, 27284-06-6; **13**, 28443-75-6; **14**, 28443-76-7; **15**, 28443-77-8; **19a**, 28443-78-9; **19b**, 28443-79-0; **20**, 28443-80-3; **21a**, 28443-81-4; **21b**, 28443-82-5; **22**, 28443-83-6; **23b**, 28443-84-7; **24**, 28443-85-8; **25a**, 28443-86-9; **25b**, 28443-87-0; **26**, 28443-88-1; **27**, 28443-89-2; **28**, 28443-90-5; **29** (X = Br), 28443-91-6; **29** (X = Cl), 28443-92-7; **30**, 28443-93-8.

(24) The very close similarity of the absorption spectrum of this species [λ_{max} (dioxane) 500 mμ, 520 (sh), 565 (sh)] to that obtained by heating **4** [λ_{max} (xylene) 505 mμ, 534 (sh), and 570 (sh)] may be noted.

Aromatic Demethoxylation in the Cyclization of 3-(β-Dialkoxyarylethylamino)phthalides to 2,3-Dihydro-7*H*-dibenzo[*de*,*h*]quinolines

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Whereas polyphosphoric acid cyclization of β-phenylethylaminophthalide (**1a**) gives lactam **3**, similar cyclizations of methylenedioxyphenyl (**1c**) and dimethoxyphenyl (**1b**) analogs proceed in the direction of respective 5,6-dialkoxy-2,3-dihydro-7-dibenzo[*de*,*h*]quinolones (**4**). In **1b** closure, the 6-methoxy group in the tetracyclic base is partly demethylated and for the most part lost, giving **4a** as the major product, together with monophenolic congener. Structure **4a** was established by spectral data, aromatization to **5**, and reduction to basic carbinol **6**, in turn further characterized as acetates **7** and **8**.

Closures of cyclic carbinolamides or enamides leading to 1-substituted (or spiro) tetrahydroisoquinoline or β-carboline acid derivatives or lactams played a prominent role in the chemistry of erythroidines[1-3] and are now well known.[4-9] These and other Pictet–Spengler closures of *N*-(β-arylethyl)enamines being our point of departure, we examined cyclizations of condensation products **1** obtained from typical primary β-arylethylamines and phthalaldehydic acid under mild conditions (azeotropic reflux, benzene or toluene).

In the first place, such products of the reaction of phthalaldehydic acid with primary amines, like those formed with secondary amines and other nucleophiles,[10] are for the most part aminophthalides **1** rather than hydroxyphthalimidines. This is apparent from their infrared spectra, in which lactone bands (5.70 μ) predominate. Further evidence for structure **1** is the fact that mild hydrogenation of **1b** and **1c** gives amino acids **2b** and **2c**, respectively, products which would not arise from hydroxyphthalimidines. By contrast, as is well known, reactions of the ring tautomeric acid chlorides

(1) B. Belleau, *J. Amer. Chem. Soc.*, **75**, 5765 (1953); *Can. J. Chem.*, **35**, 651, 663 (1967).
(2) A. Mondon, *Chem. Ber.*, **92**, 1461, 1472, 2543 (1959).
(3) V. Boekelheide, *et al.*, *J. Amer. Chem. Soc.*, **81**, 3955 (1959).
(4) S. Wawzonek and G. E. Nelson, *J. Org. Chem.*, **27**, 1377 (1962); **32**, 3618 (1967).
(5) W. I. Taylor and M. M. Robison, U. S. Patent 3,210,357 (1965).
(6) L. Berger, A. J. Corraz, and J. Lee, U. S. Patent 3,301,857 (1967).
(7) J. Shavel and G. C. Morrison, U. S. Patent 3,341,528 (1967).
(8) M. Winn and H. E. Zaugg, *J. Org. Chem.*, **33**, 3779 (1968).
(9) W. J. Houlihan and R. E. Manning, U. S. Patents 3,383,388, 3,414,585 (1968); 3,516,993 (1970).
(10) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).