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Photoisomerization of 2-Isocyano- and 2,*x*′-Diisocyanobiphenyls in Cyclohexane[1]

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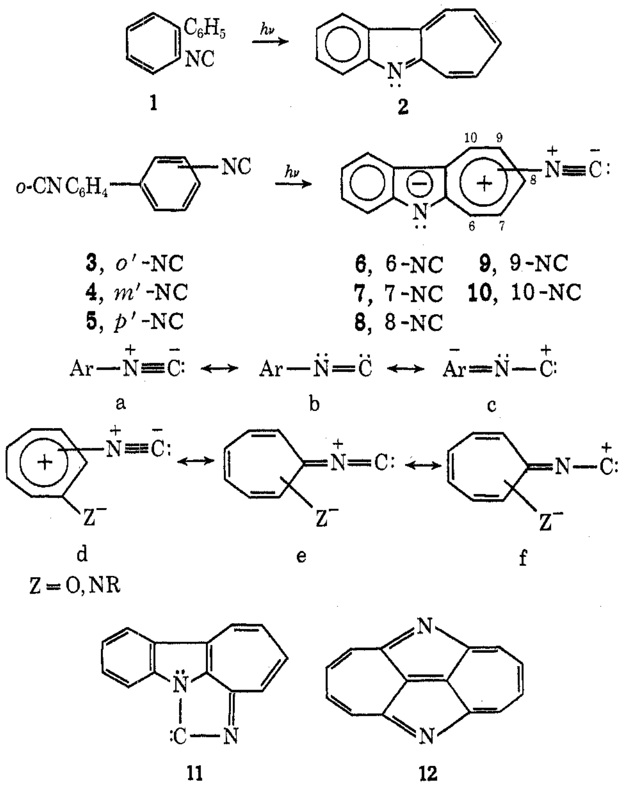
Irradiating cyclohexane solutions at 254 nm produced cyclohept[*b*]indole **2** from both 2-isocyanobiphenyl (**1**) and 2-isothiocyanatobiphenyl. Similar treatment produced 6- and 10-isocyanocyclohept[*b*]indole (**6**) (unisolated) and **10** from 2,2′-diisocyanobiphenyl (**3**); 7- and 9-isocyanocyclohept[*b*]indole (**7** and **9**) (not differentiated) from 2,3′-diisocyanobiphenyl (**4**); and 8-isocyanocyclohept[*b*]indole (**8**) from 2,4′-diisocyanobiphenyl (**5**). Cyclization of **6** accounted for properties expected of the aminoimino carbene **11** or its dimer **23**. Prolonged irradiation changed **2** into unidentified material and isomerized **1** into phenanthridine (**14**) in trace amount. Each ring enlargement has been attributed to an intramolecular attack on the adjacent phenyl group by an electrophilic carbenoid isocyano carbon. Hydrolysis converted each isocyanide into the corresponding aminocyclohept[*b*]indole.

An isomerization of 2-isocyanobiphenyl **1** into cyclohept[*b*]indole **2**[2] has been extended to the 2,*x*′-diisocyanobiphenyls **3**, **4**, and **5** (Scheme I). This has initiated an investigation of substituent effects on the benzene ring undergoing expansion and also produced the isomeric isocyanocyclohept[*b*]indoles **6**–**10** as examples of hitherto unknown isocyanocycloheptatrienes. Each of the latter could undergo a resonance coupling between the isocyano and the seven-membered aromatic ring electrons; however, for a similar interaction between an isocyano group and the benzene ring to occur, it has been suggested that strong electron withdrawal from the isocyano group might be required.[3,4] Perhaps interaction was revealed by the ir absorption of *p*-nitrophenyl isocyanide (2116 cm^{-1} from a potassium bromide pellet);[5] unfortunately, efforts to obtain a dinitro derivative with a nitro group ortho to the isocyano group have failed.[6] Presumably electron withdrawal increases electrophilicity at the isocyano carbon through greater participation from the ordinarily less significant structures b and c (Scheme I). Structure a is generally predominant and accounts for reactivity in the ground state.[7] Structures e and f would bestow electrophilic properties upon the isocyano carbon of isocyanotropones and isocyanotroponimines; comparable structures are available to each isocyanide **6**–**10**.

SCHEME I



The possibility of ring-closure isomerization gave additional significance to **6** and **10** insofar as the aminoimino carbene **11** from **6** would share with diamino carbenes the controversial property of reversible dimeriza-

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[1] Financial assistance was received from NASA Grant No. NGR 14 012 004.

[2] J. H. Boyer and J. de Jong, *J. Amer. Chem. Soc.*, **91**, 5929 (1969).

[3] L. L. Ferstandig, *ibid.*, **84**, 1323, 3553 (1962); P. v. R. Schleyer and A. Allerhand, *ibid.*, **84**, 1322 (1962); **85**, 866 (1963).

[4] I. Ugi, "Isonitrile Chemistry," Academic Press, New York, N. Y., 1971, p 5.

[5] I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

[6] Reference 4, p 14. See also G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 191 (1940).

[7] Reference 4, pp 1–7.

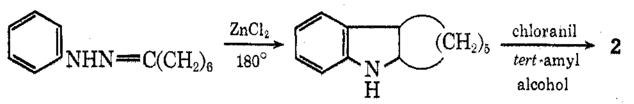
tion,[8] and a ring closure from **10** with expansion of the benzene ring would afford the unknown 5,10-diazadipleiapentalene **12**, a bridged heteroannulene with $4n + 2$ π peripheral electrons.

Results and Discussion

Isocyanides 1, 3, 4, and 5.—Each isocyanide was obtained by dehydration of the corresponding formamide with phosgene.[9] Incomplete dehydration gave 2-isocyano-2′-formamidobiphenyl and unresolved mixtures of each of 2,3′- and 2,4′-isocyanoformamides.

The minor variation in the NC stretching frequencies at 2127 cm^{-1} for **3–5** in chloroform and 2130 ± 3 cm^{-1} for nine derivatives of phenyl isocyanide in chloroform[10] agrees with reported values for aryl isocyanides in chloroform: phenyl, 2132[11] and 2136;[12] *p*-tolyl, 2136[12] and 2129.7;[13] *p*-chlorophenyl, 2136;[12] *p*-methoxyphenyl, 2140 cm^{-1}.[12] With this support for a minimal resonance between NC and C_6H_5 electrons, an NC stretching frequency at 2119 cm^{-1} for 2-isocyano-2′-formamidobiphenyl in chloroform appears exceptional. The effect of intramolecular hydrogen bonding needs to be investigated.[11,12]

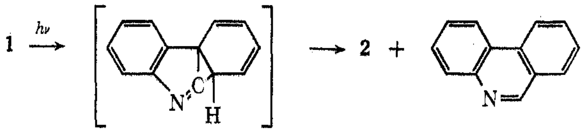
Isomerization of *o*-Isocyanobiphenyl (1).—Irradiation of *o*-biphenylyl isothiocyanate led to the dissociation of sulfur, the generation of *o*-isocyanobiphenyl (**1**), and the discovery of the isomerization **1** → **2**.[2] The latter product was independently prepared by the dehydrogenation of 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole, obtained from the phenylhydrazone of cycloheptanone by the Fisher indole synthesis,[14] and by treating 6-amino-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole with palladium on charcoal or with chloranil (see Experimental Section).



Conversion into cyclohept[*b*]indole **2** was the exclusive reaction during at least the first 5 min of irradiation of **1** in cyclohexane under either oxygen or nitrogen. After about 19 hr of irradiation, conversion under nitrogen gave cyclohept[*b*]indole **2** in 69% yield based on 76% recovery of isocyanide **1**.

A quantitative irreversible thermal isomerization of *o*-isocyanobiphenyl (**1**) in diphenyl ether at 250° into *o*-cyanobiphenyl occurred under conditions comparable to the isomerization of other aryl isocyanides into cyanides and without an intramolecular reaction with the adjacent phenyl group.[15] Achieving the latter by photoexcitation apparently depended on a withdrawal of electron density from the isocyano carbon and its electrophilic attack on the adjacent phenyl group. A favorable geometry for attack at either of the two CC bonds adjacent to the pivotal bond places the rings nearly perpendicular to each other with the carbon atom of the *o*-isocyano group directly above one or the other of the pertinent CC bonds. The reaction was assumed to proceed from an excited singlet state, since it was not quenched by oxygen (*vide ante*).

The formation of a transient "intramolecular adduct" **1a** is proposed in analogy with norcaradiene, a postulated intermediate in the formation of cycloheptatriene from carbene and benzene.[16] Toluene, a minor product, represents formal carbene insertion into a CH bond; however, rearrangement of an intermediate adduct may be responsible, since thermal isomerization of 7,7-dicyanonorcaradiene gave both phenylmalononitrile and a cycloheptatriene.[17] The generation of phenanthridine **14** in trace amount after 57 hr of irradiating *o*-isocyanobiphenyl presents a similar uncertainty which has not been resolved.[18] It is not produced from **2**, since a slow transformation of the latter into unknown material was established by an independent experiment in which cyclohept[*b*]indole could no longer be detected after 19 hr of irradiation and neither phenanthridine **14**, acridine, nor other isomers were found.[19] Regeneration of the isocyanide **1** from **1a**, analogous to the photofragmentation of cyclopropanones,[20] has not been established.



1a **14**

Isomerization of 2,*x*′-Diisocyanobiphenyl (3–5).—Localization of photoexcitation in **3–5** would be expected to increase, as rotation around the pivotal bond leads to orthogonal 2- and *x*′-isocyanobiphenyl rings. Enhanced electrophilicity at one or the other, but not both, isocyano groups would result from excitation in the appropriate plane. Just as electrophilic attack upon the adjacent phenyl group accounted for ring closure from **1**, a similar attack proposed for a 2-isocyano carbon leads to ring closure from **3–5**. The excited 3′- or 4′-isocyano group was nonproductive and apparently returned to its ground state without giving a chemical reaction, since a careful search revealed no evidence for the latter. Investigations on excited isocyano derivatives are continuing.

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(8) D. Lemal in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 701–749.

(9) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 472 (1965).

(10) We are indebted to Dr. V. T. Ramakrishnan for the ir spectra of these derivatives of phenyl isocyanide: 2-, 3-, and 4-methoxy; 3- and 4-nitro; 2,4-, 2,5-, and 3,4-dimethoxy; and 2-phenyl. Each spectrum was obtained from a chloroform solution and was calibrated against polystyrene.

(11) R. G. Gillis and J. L. Occolowitz, *Spectrochim. Acta*, **19**, 873 (1963), found that the frequency of the isocyanide fundamental stretching mode is greater and its intensity is slightly less in chloroform than in carbon tetrachloride, a behavior opposite to that of carbonyl groups in hydrogen bonding solvents.

(12) R. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961), reported consistently high frequencies. Four aryl isocyanides showed higher frequencies in chloroform than in carbon tetrachloride, but methyl isocyanide showed a much lower frequency in chloroform (2142 cm^{-1}) than in carbon tetrachloride (2169 cm^{-1}).

(13) W. D. Horrocks, Jr., and R. H. Mann, *Specrochim. Acta*, **19**, 1375 (1963).

(14) W. Treibs, R. Steinert, and W. Kirchof, *Justus Liebigs Ann. Chem.*, **581**, 54 (1953).

(15) Unpublished results. See also ref 4, Chapter 3.

(16) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971, p 227.

(17) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967).

(18) J. de Jong and J. H. Boyer, *Chem. Cmmun.*, 961 (1971), describe a photoisomerization of **1** in methanol in which sovent participation gives phenanthridine in high yield. Similar participation is unavailable to cyclohexane and other aprotic solvents.

(19) M. Comtet and H. D. Mettee, *Mol. Photochim.*, **2**, 63 (1970), describe photoisomerization of azulene into naphthalene.

(20) Reference 16, pp 15 and 37.

Results obtained from irradiating **1**, **4**, and **5** each for 5 min were compared (Table I). From **1** each of two equivalent paths in which bond cleavage occurred at one or the other of two ring CC bonds next to the pivotal bond produced **2** in 7.45% yield and 0.0188 quantum yield. Similarly, from **5** each of two equivalent paths produced **8** in 13.8% yield and 0.0345 quantum yield. Two nonequivalent paths from **4** produced **7** and **9** in total yield of 22.1% and 0.0553 quantum yield; however, one product, **7** or **9**, predominated with both a percentage yield of 15.1 and a quantum yield of 0.0378, describing the most efficient product formation. After irradiation for 45 min the total percentage yield of **7** and **9** was 30 ± 5 and after 90 min it was 45 ± 5 (determined spectroscopically by uv absorption data). After 90 min chromatography afforded the major product in 57.3% and the minor product in 16.4% yield after correcting for 45.0% recovery of starting material **4**.

TABLE I

PHOTOISOMERIZATION OF ISOCYANOBIPHENYLS, *o*-$CNC_6H_4C_6H_4R$, INTO CYCLOHEPT[*b*]INDOLES. IRRADIATION OF 10 ML OF A 2.5×10^{-3} *M* SOLUTION IN CYCLOHEXANE UNDER ORDINARY ATMOSPHERE AT 254 NM FOR 5.0 MIN

		Cyclohept[*b*]indoles						
						Yield[a]		
R	No.	No.	E^b	λ, nm[c]	ϵ^c	mol × 10^4	%	Φ × 10^2
H	**1**	**2**	0.275	527.5[d]	366[d]	3.77	14.9	3.77
m′-CN	**4**	**7** (9)	0.270	515.0	411	3.78	15.1	3.78
			0.390	600.0	296			
		7 (9)	0.270	515.0	268	1.75	7.0	1.75
			0.390	600.0	164			
p′-CN	**5**	**8**	0.460	525.0	326	6.90	27.6	6.90

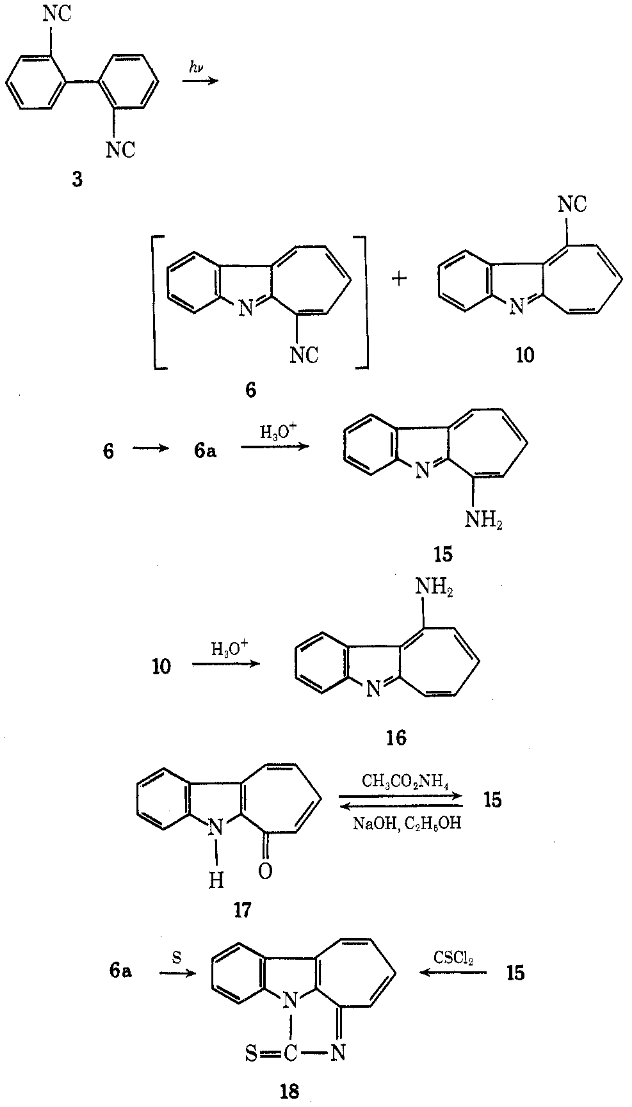
[a] The conversion of **1** → **2** was quantitative, since a 14.5 ± 0.4% decrease in the amount of **1** was determined by gc. [b] Absorbance. [c] Determined from benzene solutions. [d] A. G. Anderson, Jr., and J. Tazuma, *J. Amer. Chem. Soc.*, **74**, 3455 (1952), report absorption at 500 nm (log ε 2.61) for **2** in alcohol.

Each indole, **2**, **7**, **8**, and **9**, showed absorption near 500 nm, as expected of an azulene chromophore.[21] The NC stretching frequency for **7** and **9** at 2119 cm^{-1} and for **8** at 2114 cm^{-1} (chloroform solutions) supported electron withdrawal by a resonance coupling with the seven-membered aromatic troponimine ring system (Scheme I). Further support was found in the extremely facile hydrolysis of **7**–**9** into the corresponding aminocyclohept[*b*]indoles **20**–**22**.

The nature of the assistance from the isocyano substituent in the ring undergoing attack is incompletely understood. An absence of ground-state resonance coupling of isocyano and phenyl electrons and a predicted retardation in ring closure to a derivative of **1a** by an inductive electron withdrawal by the isocyano substituent in **4** and **5** apparently eliminated assistance in the ring-closure step. On the other hand, ring expansion into a cyclohept[*b*]indole **7**–**9** could be assisted by the stabilization of product through a resonance coupling of electrons in the aromatic seven-membered ring with those in the isocyano substituent. A correlation between the substituent position and the extent of stabilization appears to place position 8 between 7 and 9, one of which is more effective than the other. Further investigations with a variety of electron-donating and withdrawing substituents are needed.

Irradiation of 2,2′-diisocyanobiphenyl (**3**) apparently produced 6- and 10-isocyanocyclohept[*b*]indoles. While further changes to undetected **6**, concerted with or subsequent to its formation, gave a new product **6a**, no evidence for the isomerization **10** → **12** was found. Separation of the product mixture on a silica gel column changed **6a** into an amine **15** (Scheme II), also produced by treating an ether solution of **6a** with 2 *N* hydrochloric acid. In a similar way the isocyanide **10** was transformed into an amine **16**, isomeric with **15**. The identification of **15** as 6-aminocyclohept[*b*]indole was established by its preparation from cyclohept[*b*]indol-6(5*H*)-one (**17**) and ammonium acetate[22] and by the regeneration of the ketone **17** on treating the amine **15** with alcoholic alkali (Scheme II).

SCHEME II



Sulfur, ethanol, aniline, and water each revealed the nucleophilicity of **6a**. At room temperature sulfur, added to the product mixture of **3**, **10**, and **6a**, slowly combined with **6a**. A 1:1 adduct was identical with a cyclic thiourea **18** also prepared by treating the amine

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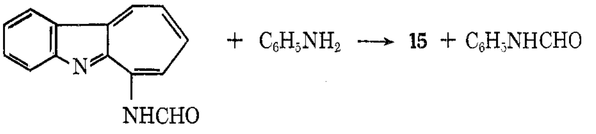
(21) A. G. Anderson, Jr., and J. Tazuma, *J. Amer. Chem. Soc.*, **74**, 3455 (1952), report absorption at 500 nm (log ε 2.61) for **2** in alcohol.

(22) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 339.

15 with thiophosgene (Scheme II), otherwise noteworthy for the lack of formation of the ring-opened isomer, 6-isothiocyanatocyclohept[*b*]indole. There was no reaction between sulfur and either of the isocyanides **3** and **10**.

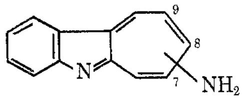
Addition of a few drops of absolute ethanol to the product mixture **3**, **10**, and **6a** brought about an immediate color change from violet to yellow-red. A reaction with **6a** is assumed since the isocyanide **10** was detected after the addition of ethanol by absorption near 500 nm and was isolated chromatographically from silica. A slower reaction with aniline was found by uv monitoring to be complete after 60 hr. The usual chromatographic separation from silica gave the isocyanides **3** and **10**, formanilide, 6-aminocyclohept[*b*]indole (**15**), and 6-anilinocyclohept[*b*]indole (a tentative assignment). The greater resistance of 10-isocyanocyclohept[*b*]indole (**10**) to aniline was established by an independent experiment. In the related facile hydrolysis of **6a**, 6-formamidocyclohept[*b*]indole (**19**) was formed. By acid or base hydrolysis and by thermal decarbonylation it was transformed into the amine **15**. Apparently formanilide resulted from an amide interchange between **19** and aniline.



19

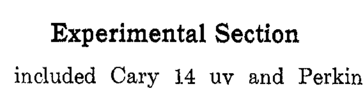
As expected 10-isocyanocyclohept[*b*]indole resembles its isomers **7**–**9** insofar as its NC stretching frequency at 2109 cm^{-1} (chloroform) supports resonance coupling of NC and the seven-membered aromatic ring electrons. The extent of the bathochromic shifts from reference values at 2130 ± 3 cm^{-1} alternates with the positions of the isocyano substituent so that the shifts for **7** and **9** are less than those for **8** and **10**. Presumably this is related to a charge alternation for the carbon atoms of the aromatic seven-membered ring.[23]

An alternation of color for the aminocyclohept[*b*]indoles gave blue to **20** and **22** and yellow-orange to **15**, **21**, and **16**.[24] The basicities of cyclohept[*b*]indole, pK_a = 6.7, and its 6-, 7-, 8-, 9-, and 10-amino derivatives, **15**, **20**, **21**, **22**, and **16**, respectively, pK_a = 7.8–9.7, are considerably higher than those of isomeric acridine, pK_a = 5.6, and its 6-, 7-, 8-, and 9-amino derivatives, pK_a = 4.4–8.04,[25] and phenanthridine, pK_a = 3.30, and its 6- and 9-amino derivatives, pK_a = 6.88,[26] 7.31.[25] These are expected results from an electron release required for aromaticity in the seven-membered ring.



20, 7(or 9) NH_2
21, 8 NH_2
22, 7(or 9) NH_2

While certain properties of **6a** are descriptive of 6-isocyanocyclohept[*b*]indole, both the ring-closure isomer, an aminoimino carbene **11**, and the dimer olefin **23** might accommodate better the enhanced nucleophilicity at the "isocyano" carbon and the absence of an NC stretching frequency in the region 2110–2140 cm^{-1}. Attributing nucleophilicity in the related structure to the diamino carbene monomer **24**, and later corrected to the tetraaminoethylene dimer **25**,[8] tends to suggest a similar property for **23**, but confirmation of the relationship between **6** and **23** needs further investigation.



23

$(R_2N)_2C$: $(R_2N)_2C{=}C(NR_2)_2$
24 **25**

Experimental Section

Instruments included Cary 14 uv and Perkin-Elmer 237B grating ir spectrophotometers; Varian A-60 nmr and Perkin-Elmer 270 masss pectrometers; Barber-Coleman flame ionization gc Model 5320 equipped with an 8 × 0.25 in. steel coil packed with 5% Ge-Xe-60 Chromosorb G, 60–80 AW DMGS (Nuclear Chicago), operated with a column temperature of 210–220°, injection port about 250°, and detector about 280°, nitrogen carrier gas flow rate of 60–70 ml min^{-1}; and a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with 16 low-pressure mercury 254-nm lamps.

Before irradiation under nitrogen, solutions were degassed with a stream of nitrogen. Spectrograde cyclohexane was distilled from lithium aluminum hydride directly into the quartz reactor tube. J. T. Baker silica gel was used in column chromatography. Melting points and boiling points are uncorrected. Yields are based on recovered starting material. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Ill.

Structure assignments for **2**, **14**, **15**, **17**, **18**, and each recovered starting material have been based on identical comparisons with corresponding authentic samples by examining two or more physical properties including ir, uv, nmr, tlc, n_D, and mixture melting point. The molecular weight for *o*-isothiocyanatobiphenyl, **1**–**5**, **7**–**10**, and **14**–**22** was confirmed by the mass spectrum M$^+$ from *m/e* at 70 eV for each compound. The M$^+$ 194 for **21** was confirmed by *m/e* at 12 eV for **21**·HCl.

The NC stretching frequencies for eight isocyanides were measured in chloroform: **1**, 2130; **3**, 2128; **4**, 2127; **5**, 2126; **7**, 2119; **8**, 2114; **9**, 2119; and **10**, 2109 cm^{-1}.

By means of a Sargent-Welch pH meter, Model LS, pK_a values were determined from the titration curve at half-neutralization of about 20 mg of each base in 25 ml of 50% aqueous methanol by 0.05 *N* hydrochloric acid at 26–27° under nitrogen: **2**, 6.7; **15**, 7.8; **20** (or **22**), 9.2; **21**, 9.7; **20** (or **22**), 9.7; **15**, 9.3. The relatively low p*K* of 7.8 for **15** may be the result of intramolecular hydrogen bonding between the two amino nitrogen atoms.

Quantum Yields.—Samples (10 ml) of the standard actinometer solution of potassium ferrioxalate[27] were subjected to three freeze–thaw cycles (liquid nitrogen, vacuum line at 2 × 10^{-5} mm). They were then irradiated in small quartz tubes placed in a merry-go-round assembly in a Rayonet reactor equipped with 16 mercury low-pressure lamps emitting at 254 nm. After an irradiation time of 30.0 and 60.0 sec, conversions into ferrous ions of 1.25 × 10^{-3} and 2.50 × 10^{-3} *M*, respectively, were found. From the quantum yield (1.25) the calculation of the intensity of the absorbed light was found to be 2.0 × 10^{16} quanta sec^{-1} cc^{-1}. Each diisocyanobiphenyl in cyclohexane (10 ml, 2.5 × 10^{-3} *M*) was similarly irradiated for 5.0 min but in the presence of atmospheric oxygen. After evaporation of the

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[23] A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Table of Molecular Orbital Calculations," Pergamon Press, Oxford, 1965, p 305.

[24] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc., Ser. A*, **278**, 64 (1964), have shown that color alteration in azulene derivatives is mainly the result of the inductive effect of the substituent.

[25] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948).

[26] V. de Gaouck and R. J. W. Le Fevre, *ibid.*, 1392 (1939).

[27] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956); C. A. Parker, *ibid.*, **220**, 104 (1953).

solvent the residue was dissolved in 5 ml of benzene and the yield of insertion products was determined spectrophotometrically. A yield of 14.9% of cyclohept[*b*]indole was calculated from λ_{max} 527.5 nm (ϵ 366), whereas a loss of 14.5 ± 0.4% of *o*-isocyanobiphenyl was calculated from integrated areas of several gas chromatograms compared with gas chromatograms from the standard solution. Results are found in Table I.

***o*-Isothiocyanatobiphenyl.**—To a solution of 20.60 g (0.10 mol) of dicyclohexylcarbodiimide in 20 ml of pyridine and 40 ml of carbon disulfide cooled to −10°, a solution of 16.9 g (0.10 mol) of *o*-aminobiphenyl in 20 ml of pyridine was added dropwise with stirring, which was continued for 3 hr at −10 to 0° and for 18 hr at room temperature. A nearly quantitative yield of 1,3-dicyclohexylthiourea, mp 178–181°, was isolated after concentration and treatment with cold ether. Eluting the concentrated filtrate from silica with *n*-hexane followed by distillation gave *o*-isothiocyanatobiphenyl as a colorless, viscous liquid: yield 15.8 g (75.0%); bp 130–132° (0.25 mm); $n^{26}\text{D}$ 1.6805; ir (neat) 2100 cm^{-1} (NCS); nmr (CDCl$_3$) δ 7.35 (m). *Anal.* Calcd for $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63; S, 15.18. Found: C, 74.25; H, 4.49; N, 6.75; S, 15.00.

Isocyanides.—Following general procedures,[9] formamides were dehydrated by phosphorus oxychloride or with phosgene into corresponding isocyanides. 2-Isocyanobiphenyl (1)[28] was obtained in 65% yield, bp 113–114° (1.5 mm), $n^{21.5}\text{D}$ 1.6115. *Anal.* Calcd for $C_{31}H_9N$: C, 87.12; H, 5.06; N, 7 82. Found: C, 87.17; H, 5.32; N, 7.88.

2,2′-Diisocyanobiphenyl (**3**) was obtained in 29% yield, mp 110.5–112° (lit.[9] mp 101–104°). *Anal.* Calcd for $C_{14}H_8N_2$: C, 82.32; H, 3.95; N, 13.73. Found: C, 82.28; H, 3.95; N, 13.76.

The half-converted by-product, 2-isocyano-2′-formamidobiphenyl, obtained in 27% yield, recrystallized from ethanol as a colorless solid: mp 106–107.5°; ir (CHCl$_3$) 3378 (NH), 2119 (N≡C), 1695 cm^{-1} (C=O). *Anal.* Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61; O, 7.19. Found: C, 75.39; H, 4.46; N, 12.61; O, 7.43.

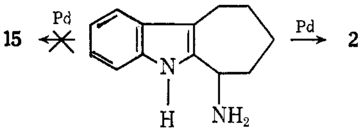
2,3′-Diisocyanobiphenyl (**4**) was obtained in 54% yield, mp 145–146°. *Anal.* Calcd for $C_{14}H_8N_2$: C, 82.37; H, 3.95; N, 13.72. Found: C, 82.32; H, 4.09; N, 13.55.

2,4′-Diisocyanobiphenyl (**5**) was obtained in 39% yield, mp 94.5–95.5° (lit.[9] mp 97–98°).

Irradiation of *o*-Isothiocyanatobiphenyl.—A solution of 1.240 g (5.90 mmol) of *o*-isothiocyanatobiphenyl in 400 ml of cyclohexane was flushed with nitrogen for 3 hr and irradiated at 254 nm for 64 hr under a stream of nitrogen. Cyclohexane was removed and the residue, chromatographed on silica, gave 9 mg of sulfur, 24%, mp and mmp 117–119°, eluted with *n*-hexane; 1.030 g of starting material, 83.0%, eluted with *n*-hexane–benzene (10:1); 44.5 mg of *o*-isocyanobiphenyl (**1**), 25%, eluted with *n*-hexane–benzene (3:2); and 50 mg of cyclohept[*b*]indole **2**, 28%, eluted with chloroform–ether (4:1), mp 134.5–136° (sealed tube) (lit.[14] mp 143°), methiodide mp 232°.[14] *Anal.* Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 86.91; H, 5.16; N, 7.61. Unidentified fractions were obtained on eluting with *n*-hexane–benzene, benzene–chloroform, and chloroform–ether but neither carbazole (ring closure product from *o*-biphenylyl nitrene, if present) nor phenanthridin-6(5*H*)-one was detected.

Irradiation of *o*-Isocyanobiphenyl (1).—A solution of 540 mg (3.0 mmol) of *o*-isocyanobiphenyl in 400 ml of cyclohexane was irradiated under either oxygen or nitrogen at 254 nm. After about 3 hr the isomerization under nitrogen became slower, as a coating of unknown material had accumulated on the walls of the reaction flask. In contrast the flask containing the reaction under oxygen remained clear. Upon replacing the nitrogen atmosphere with oxygen in the fouled flask, continued irradiation slowly cleared away the heavy coating and after 6–7 hr the formation of **2** restarted. The formation of **2**, monitored by absorption near 500 nm[21] for aliquots taken at intervals, reached a maximum after 19 hr of irradiation. At that time chromatographic separation of the mixture from silica gave starting material, eluted by *n*-hexane–benzene (3:2), 376 mg (69.5%) followed by elution of **2** with chloroform–ether (3:1), 103 mg (62.8%). Chromatography after 57 hr afforded 62.8% of starting material, less than 1% of phenanthridine **14**, eluted with benzene–chloroform (1:3), and 42% of **2** eluted with chloroform. Examination of the crude reaction mixture after irradiation under oxygen (air) did not reveal the formation of either *o*-isocyanatobiphenyl or phenanthridin-6(5*H*)-one. After 19 hr of irradiation under nitrogen, cyclohept[*b*]indole **2** was completely transformed into unknown material; however, phenanthridine **14** could not be detected.

Cyclohept[*b*]indole (2).—To a stirred refluxing solution of 5.0 g (27.0 mmol) of 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole, mp 142–143.5°,[21] in 100 ml of *tert*-amyl alcohol, 15 g (61.0 mmol) of powdered chloranil, mp 290°, was added in small portions. Refluxing was continued for 6 hr. The cooled solution, diluted with ether, was extracted with 2 *N* sodium hydroxide and with 2 *N* hydrochloric acid. The yellow acidic aqueous layer was washed with ether and cyclohexane. Basifying, extracting with cyclohexane, drying (Na$_2$SO$_4$), concentrating, and recrystallizing afforded 55 mg (1.0%) of authentic cyclohept[*b*]indole **2**. An attempted dehydrogenation of 6-amino-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (*vide infra*) with palladium on charcoal gave a trace of **2**, but 6-aminocyclohept[*b*]indole **15** could not be found.



Irradiation of 2,2′-Diisocyanobiphenyl (3).—A solution of 250 mg (1.23 mmol) of **3** in 400 ml of cyclohexane was irradiated at 254 nm for 4 hr under nitrogen. Cyclohexane was removed. The residue separated from a column of silica gel to give the fractions (compound, milligrams, per cent yield, eluting solvent): **3**, 44, 17.6, *n*-hexane–benzene (1:4); **19**, as a red solid, 3, 1.2, benzene–chloroform (4:1); **10**, 55, 26.7, benzene–chloroform (1:1); and **15**, 84, 42.9, ether–ethanol (4:1). Recrystallization of the formamide **19** from *n*-hexane gave small, deep red needles: mp 115–140° dec; ir (CHCl$_3$) 3279 (m), (NH), 1704 cm^{-1} (C=O); nmr (CDCl$_3$) δ 9.87 (s, 1, NH), 9.00 (s, 1, O=CH), 9.30 (d, 1, J = 11 Hz), 8.85 (d, 1, J = 8 Hz), 8.6–7.3 (m, 6). It did not give a satisfactory elementary analysis. When heated at 145° for 10 min the formamide **19** lost carbon monoxide to give the corresponding amine **15**. Shaking a solution of **19** in diethyl ether for 90 sec with aqueous 0.25 *N* sodium hydroxide also converted it into **15**, but shaking a basic aqueous solution (pH 10) for 10 min had no effect.

From cyclohexane, 10-isocyanocyclohept[*b*]indole (**10**) recrystallized as long, violet needles: mp >300° (becoming black); nmr (CDCl$_3$) δ 8.95 (d, 1, J = 8 Hz), 8.63 (m, 1), 8.30–7.37 (m, 6). *Anal.* Calcd for $C_{14}H_8N_2$: C, 82.37; H, 3.95; N, 13.72. Found: C, 81.80; H, 3.97; N, 13.65.

Recrystallization of the fourth fraction from carbon tetrachloride gave 6-aminocyclohept[*b*]indole (**15**) as an orange solid: mp 179–180° (sealed tube) after sublimation at 160–180° (15 mm); nmr (CDCl$_3$) δ 8.60 (d, 1, J = 10 Hz), 8.27 (d, 1, J = 8 Hz), 8.01–6.93 (m, 6), 6.01 (s, 2, NH$_2$). *Anal.* Calcd for $C_{13}H_{10}N_2$: C, 80.37; H, 5.15; N, 14.43. Found: C, 80.48; H, 5.14; N, 14.59.

In another run after irradiation for 1 hr, the solvent was removed. Extraction of the product mixture with a minimum amount of dry ether separated the isocyanides **3** and **10** from **6a**, a shiny black amorphous solid which resisted purification and did not show the strong isocyano ir absorption band in the region 2100–2150 cm^{-1}. An ether solution of the residue was extracted with 2 *N* hydrochloric acid. Starting material, 16.5%, was recovered from the ether layer. Ether extraction of the cooled aqueous layer, after neutralization with 2 *N* sodium hydroxide to pH 6–7, gave the amine **15**, 46%. Further treatment of the aqueous layer with base and extraction with ether gave 10-aminocyclohept[*b*]indole (**16**), 28.4%, insoluble in *n*-hexane, cyclohexane, and benzene, slightly soluble in chloroform, and soluble in methanol and ethanol. It was not satisfactorily recrystallized and was apparently too basic for elution from silica gel by the usual solvents. It was eluted by mixtures of methanol and ether from basic aluminum oxide and isolated as a solid: mp >200°; nmr (DMSO-d_6) δ 8.97 (d, 1, J = 8 Hz), 8.83–7.37 (m, 7). A picrate derivative was prepared and recrystallized from 10% aqueous acetic acid and from ethanol as yellow needles, mp 229–230°. *Anal.* Calcd for $C_{19}H_{13}N_5O_7$: C, 53.91; H, 3.09; N, 16.55. Found: C, 53.61; H, 3.20; N, 16.23.

To the deep red-violet solution obtained after 4 hr of irradiation of 200 mg (1.0 mmol) of **3**, 100 mg (3.1 mmol) of sulfur was added

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[28] Previously reported as a solid, mp 116–118°.[9]

and the solution was stirred for 60 hr under nitrogen as a red solid precipitated. Extraction of the product mixture in ether with an aqueous 2 *N* hydrochloric acid solution removed starting material and unreacted sulfur. The crude cyclic thiourea **18**, 71 mg (30.7%), was obtained from the aqueous layer after neutralizing with aqueous sodium hydroxide to pH 5, extracting with ether, drying (Na_2SO_4), filtering, and removing ether. The material was purified by elution from basic aluminum oxide with benzene–chloroform (1:1) and recrystallization from carbon tetrachloride–ethanol (1:1) as orange-red needles: mp 208° dec; ir ($CHCl_3$) 1661, 1582 cm^{-1}; nmr (DMSO-d_6) δ 7.43–8.87 (m). *Anal.* Calcd for $C_{14}H_8N_2S$: C, 71.14; H, 3.41; N, 11.86. Found: C, 70.94; H, 3.54; N, 11.84.

Cyclic Thiourea 18 from 6-Aminocyclohept[*b*]indole (15).—To a solution of 50.0 mg (0.258 mmol) of **15** in 10 ml of anhydrous methylene chloride and 1 ml of triethylamine 3 drops of condensed thiophosgene was added. The mixture was heated at reflux for 0.5 hr, cooled in an ice bath, diluted with 50 ml of ether, and extracted with 2 *N* hydrochloric acid. After basifying with 2 *N* sodium hydroxide, extracting with ether, drying (Na_2SO_4), and removing the solvent, 16 mg of material was obtained and separated by preparative thin layer chromatography (Chromar Sheet 1000, Mallinckrodt). Elution with chloroform–ethanol (4:1) gave a solid identical with the thiourea **18**, 9 mg (14.7%).

6-Amino-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole.—As previously reported, 6-oxo-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole recrystallized from benzene as yellow plates: mp 149–151°;[29] ir ($CHCl_3$) 3436 (NH), 1626 cm^{-1} (C=O); nmr ($CDCl_3$) δ 9.46 (1, NH), 7.72–6.87 (m, 4, aromatic), 3.07 (m, 2, CH_2CO), 2.82 (m, 2, $=CCH_2-$), 1.96 [m, 4, $(CH_2)_2$]. The oxime derivative recrystallized from benzene–hexane and from carbon tetrachloride as colorless needles and prisms, mp 126.5–128.5°. *Anal.* Calcd for $C_{13}H_{14}N_2O$: C, 72.87; N, 6.59; N, 13.08. Found: C, 73.13; H6.64; N, 13.28.

A solution of 200 mg (0.935 mmol) of the oxime in 100 ml of dry ether was refluxed for 3 hr with 100 mg of lithium aluminum hydride. Inorganic hydroxides were precipitated by adding 3 drops of water, 9 drops of 2 *N* sodium hydroxide, and again 3 drops of water. The colorless ether filtrate was dried (Na_2SO_4) and the ether was removed. A sticky residue gave, upon trituration with carbon tetrachloride, 46 mg (25.7%) of 6-amino-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole as colorless crystals, mp 111–112° after recrystallization from carbon tetrachloride, mass spectrum M^+, 70 eV, *m/e* 200. *Anal.* Calcd for $C_{13}H_{16}N_2$: C, 77.94; H, 8.06; N, 13.99; mol wt, 200.29. Found: C, 77.77; H, 8.02; N, 13.92.

Cyclohept[*b*]indol-6(5*H*)-one (17).—A mixture of 195 mg (1.0 mmol) of 6-keto-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole[29] and 64 mg (2.0 mmol) of sulfur in a 3-ml tube provided with a condenser and gas outlet on top was immersed in a Wood's metal bath kept at 235°. Within 7 min 48.5 ml of gas was collected in a gas buret. After cooling, a black solid was triturated with 6 *N* hydrochloric acid. The acidic solution was filtered, cooled in ice, and neutralized with aqueous 6 *N* sodium hydroxide. A yellow precipitate was collected, dried, and sublimed at 220–230° (15 mm) to give 55 mg (28.0%) of **17** as bright yellow needles: mp 249.5–250.5°; ir ($CHCl_3$) 3413 (NH), 3175 (intramolecular H bonding), 1618 (C=O); nmr (DMSO-d_6) δ 12.7 (s, 1, NH), 8.38 (m, 2), 7.87–6.87 (m, 6). *Anal.* Calcd for $C_{13}H_9NO$: C, 79.97; H, 4.65; N, 7.18. Found: C, 79.93; H, 4.49; N, 7.28.

In an alternative preparation a solution of 60 mg (0.31 mmol) of 6-aminocyclohept[*b*]indole **15** and 170 mg of sodium hydroxide in 4 ml of ethanol–water (1:1) was heated under reflux for 15 hr. The solution was cooled and diluted to 25 ml with water and extracted with methylene chloride. The organic layer was dried (Na_2SO_4) and put on a silica column. Chloroform eluted 45 mg (74.5%) of **17**.

6-Aminocyclohept[*b*]indole (15).—A mixture of 100 mg (0.5 mmol) of **17**, 5 g of ammonium acetate, and 3 ml of acetic acid was refluxed for 10 hr. Dilution with water precipitated 75 mg (75%) of **17**. The filtrate was basified, extracted with ether, dried (Na_2SO_4), and filtered. Removal of the solvent left about 5 mg of a red solid. Heating for 90 min at 85–90° in 2 *N* hydrochloric acid afforded a trace of **15** after the usual work-up.

Irradiation of 2,3′-Diisocyanobiphenyl (4).—A solution of 200 mg (1.0 mmol) of **4** in 400 ml of cyclohexane was irradiated for 1.5 hr under conditions similar to those described above. Analysis of the uv absorption for a sample taken after 45 min revealed a conversion into **7** and **9** of 30 ± 5% and after 90 min of 45 ± 5%. In the usual work-up 90 mg (45%) of starting material was eluted from silica with *n*-hexane–benzene (1:1). The isomers **7** and **9** were apparently separated by elution with benzene–chloroform (1:1). The one in lower yield, 18 mg (16.4%), eluted first and recrystallized from benzene as transparent violet plates, mp >280° (darkening above 210°). *Anal.* Calcd for $C_{14}H_8N_2$: C, 82.37; H, 3.95; N, 13.72. Found: C, 82.46; H, 4.06; N, 13.88. The major product, 63 mg (57.3%), recrystallized from cyclohexane as tiny, dark brown needles, mp >280°. *Anal.* Found: C, 82.07; H, 4.17; N, 13.58. An isomeric rather than an identical relationship between the minor product A (**7** or **9**) and the major product B (**7** or **9**) was best established by ir ($CHCl_3$) and supported by less decisive differences in the uv max (C_6H_6) and mass spectral [70 eV, *m/e* (rel intensity)] values, all obtained from analytically pure samples: A, ir 2119 (s), 1608 (s), 1595 (s), 1439 (m), 1404 (m), 1337 (m), and 915 cm^{-1} (s); uv 514 nm (ϵ 280), 412 (1900), 389 (4200), 373 (4600), 314 (33,000) and 302 (36,000); mass spectrum 205 (23), 204 (100), 203 (26), 178 (13), 177 (31), 176 (16), 102 (15), and 88.5 (18); B, ir 2119 (s), 1609 (s), 1484 (s), 1433 (s), 1410 (s), 1381 (s), 1368 (m), and 908 (s); uv 518 nm (ϵ 410), 410 (2400), 389 (4500), 362 (4700), 332 (16,600), and 322 (20,000); mass spectrum 205 (18), 204 (100), 203 (24), 178 (13), 177 (27), 176 (9), 102 (9), and 88.5 (7).

Each isomer **7** and **9** was hydrolyzed to the corresponding amine by shaking its methylene chloride solution with aqueous 2 *N* hydrochloric acid. The organic layer decolorized rapidly and the aqueous layer turned orange. Basifying with aqueous 2 *N* sodium hydroxide and shaking decolorized the aqueous layer and produced an intense blue color in the methylene chloride layer. Removing methylene chloride left the crude amine. Each amine **20** and **22** melted above 220° and was insoluble in *n*-hexane, benzene, and cyclohexane, slightly soluble in chloroform, and soluble in methylene chloride, methanol, or ethanol. Purification by recrystallization was unsatisfactory. Neither amine was eluted from silica gel with the usual organic solvents, but diethyl ether–methanol mixtures eluted each from basic aluminum oxide. The hydrochloride of the amine derived from the major product B crystallized as orange needles from aqueous 2 *N* hydrochloric acid and was recrystallized from methanol–aqueous 2 *N* hydrochloric acid (1:1), mp >280°. *Anal.* Calcd for $C_{13}H_{11}N_2Cl \cdot 1.75H_2O$: C, 59.54; H, 4.23; N, 10.68. Found: C, 59.54; H, 4.81; N, 10.66. *Anal.* Calcd for $C_{13}H_{11}N_2Cl$: C, 67.68; N, 4.81; N, 12.14. Found: C, 66.82; H, 4.72; N, 12.13 after drying to constant weight.

Irradiation of 2,4′-Diisocyanobiphenyl (5) in Cyclohexane.—A solution of 200.0 mg (1.0 mmol) of **5** in 400 ml of cyclohexane was irradiated for 1.5 hr. During the irradiation aliquots were taken after 45 and 90 min. The solvent in each aliquot was evaporated and the residue was dissolved in 5 ml of benzene. Absorption (benzene) at 525 nm (ϵ 326) revealed conversion into **8** of 62 and 73%, respectively. Irradiation was stopped after 90 min, and concentration of the solution gave 93 mg of **8** as black needles. After the concentrated filtrate was put on silica, elution with *n*-hexane–benzene (2:3) yielded 43 mg (21.5%) of **5**. A dark band eluted with benzene–chloroform (1:1) to give a trace of a semisolid unidentified material, ir ($CHCl_3$) 2123 cm^{-1} (N≡C). A fraction of **8**, 32 mg, was eluted with benzene–chloroform (1:1), bringing the yield of **8** to 125 mg (78%). An analytical sample of **8** was obtained upon recrystallizing from benzene as long , transparent, faintly violet plates which turned brown at 170° and gave no further change on heating to 320°, nmr ($CDCl_3$) δ 9.13–7.66 (m). *Anal.* Calcd for $C_{14}H_8N_2$: C, 82.37; H, 3.95; H, 13.72. Found: C, 82.52; H, 4.19; N, 13.88.

8-Aminocyclohept[*b*]indole.—A solution of 31.6 mg (0.15 mmol) of **8** in 50 ml of benzene was shaken in a separatory funnel with 50 ml of aqueous 2 *N* hydrochloric acid for 2 min. The deep violet color of **8** in benzene disappeared rapidly and the aqueous acid layer turned deep yellow. The layers were separated and the organic layer was again shaken with 20 ml of acid. The acid solution was basified and extracted with methylene chloride. The organic layer was dried (Na_2SO_4) and filtered. Concentrating the methylene chloride solution gave 29 mg (96.5%) of the amine as tiny yellow needles. It was eluted with methanol

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[29] M. Muhlstädt and W. Treibs, *Justus Liebigs Ann. Chem.*, **608**, 38 (1957).

from basic aluminum oxide and after solvent concentration afforded yellow needles, mp 174° dec, nmr (DMSO-d_6) δ 8.96 (d, 1, J = 11 Hz), 8.66 (m, 2), 8.2 (d, 1, J = 8 Hz), 8.01–7.47 (m, 3), 7.27 (d, 1, J = 11 Hz), each peak a doublet with J = 2 Hz. The hydrochloride was prepared by shaking a benzene solution of 60 mg (0.29 mmol) of **8** with 50 ml of aqueous 2 N hydrochloric acid. The acidic solution was allowed to stand overnight and yielded 42 mg (54.5%) of the salt as tiny, bright yellow needles, mp >280°. *Anal.* Calcd for $C_{13}H_{11}N_2Cl$: C, 67.68; H, 4.81; N, 12.14. Found: C, 67.20; H, 4.73; N, 11.76 (12.03).

Registry No.—**1**, 3128-77-6; **2**, 246-06-0; **3**, 950-95-8; **4**, 36146-64-2; **7**, 36118-87-3; **8**, 36118-88-4; **9**, 36118-89-5; **10**, 36118-90-8; **15**, 36146-65-3; **16** picrate, 36146-66-4; **17**, 35704-54-2; **18**, 36146-68-6; **19**, 36146-69-7; **20** HCl, 36146-70-0; **22** HCl, 36146-71-1; 1,3-dicyclohexylthiourea, 1212-29-9; 2-isocyano-2′-formamidobiphenyl, 36146-72-2; 6-oxo-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole oxime, 36146-73-3; 6-amino-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole, 36146-74-4; 8-aminocyclohept[*b*]indole, 36146-75-5; 8-aminocyclohept[*b*]indole hydrochloride, 36146-76-6.

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Stereochemistry of Nucleophilic Addition Reactions. The Addition of Thiophenol and of Hydrogen Chloride to 4-*tert*-Butyl-1-cyanocyclohexene

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The addition of thiophenoxide ion to 4-*tert*-butyl-1-cyanocyclohexene (**1**) in ethanol gives the two products **2** and **3** containing an axial thiophenoxy group. In tetrahydrofuran, **14** is also formed. The stereochemistries of the products were established by a combination of nmr spectroscopy, chemical transformations, and equilibration experiments. An explanation is proposed for the observed steric course of the addition. *r*-1-*tert*-Butyl-*t*-3-phenylsulfonyl-*c*-4-phthalimidomethylcyclohexane was found to be somewhat more stable thermodynamically than the *r*-1,*c*-3,*c*-4 isomer (**13**). The data suggest that the *r*-1,*t*-3,*c*-4 isomer exists predominantly in the twist–boat conformation (**12**). Severe repulsive gauche interactions between the $PhSO_2$ and the phthalimidomethyl group are proposed to explain the observed order of stabilities. The addition of HCl to **1** gives only *r*-1-*tert*-butyl-*t*-3-chloro-*t*-4-cyanocyclohexane in which the chlorine is axial.

The stereochemistry of the Michael and Michael-type additions to activated olefins of rigid conformation has been the object of study in our laboratories. We have already established that, under conditions of kinetic control, the diethyl malonate anion in ethanol solution adds to 4-*tert*-butyl-1-cyanocyclohexene to give the addition product with the equatorial malonate and axial cyanide group as the main isomer, with the (e)-malonate (e)-nitrile as the minor product.[1] Under conditions of thermodynamic control, the latter was the main product. No axial malonate could be detected, though small amounts of the product of "abnormal" Michael addition, ethyl *r*-1-*tert*-butyl-*t*-3-carbethoxymethyl-*c*-4-cyano-*t*-4-cyclohexanecarboxylate were isolated, resulting from the rearrangement of the initially formed axial malonate anion intermediate. In a nonprotic solvent, the main product was that of "abnormal" addition.

To determine whether or not the behavior of the malonate anion was representative of the mode of addition of nucleophiles in general, we embarked on a study of the addition of thiols to activated olefins chosen such that the products would have an unambiguous stereochemistry and that product mixtures could be resolved readily, the stereochemistry of the isomers established, and the isomer ratios determined quantitatively with ease. The additions of nucleophiles have been shown to be of considerable biological importance and are thought to be involved in such diverse phenomena as the carcinogenicity of α,β-unsaturated lactones,[2] carcinostatic activity of certain plant extracts,[3] stimulation of nerve endings,[4] isomerization of retinal in the visual process,[5] the action of oral contraceptives,[6] and the bacteriostatic activity of naphthoquinones.[7] It is obvious that a knowledge of the steric course of such additions could lead to the design of molecules which could better approach and fit into the active site of the biologically important molecules.

The addition of *p*-toluenethiol to 1-*p*-tolylsulphonylcyclohexene under mildly basic conditions gave mainly the thermodynamically less stable cis isomer, namely *cis*-2-*p*-tolylmercapto-1-*p*-tolylsulfonylcyclohexane.[8] Since chair–chair interconversion can occur in the final products, however, nothing can really be said definitely about the preferred mode of approach of the thiolate anion in this system under conditions of kinetic control. In contrast to the above reaction, addition of *p*-toluenethiolate to 1-*p*-tolylsulfonylcyclopentene gave the trans product, which was explained on the basis of steric interaction between the arylsulfonyl group and the arylmercapto group in the cyclopentyl intermediate anion.[9]

When thiophenoxide ion was added to 4-*tert*-butyl-1-cyanocyclohexene (**1**) in ethanol two products were formed which were resolved by gas chromatography

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