

- (3) C. Galli, G. Illuminati, and L. Mandolini, *J. Am. Chem. Soc.*, **95**, 8374 (1973).
- (4) H. Freundlich and co-workers, and G. Salomon, quoted by G. Salomon, *Trans. Faraday Soc.*, **32**, 153 (1936); see also, G. Salomon, *Helv. Chim. Acta*, **19**, 743 (1936).
- (5) M. Stoll and A. Rouve, *Helv. Chim. Acta*, **17**, 1283 (1934); **18**, 1087 (1935).
- (6) K. Ziegler, A. Lüttringhaus, and K. Wohlgemuth, *Justus Liebigs Ann. Chem.*, **528**, 162 (1937). This reaction has been reinvestigated by us in great detail. See previous papers in this series.
- (7) C. Galli and L. Mandolini, *Gazz. Chim. Ital.*, **105**, 367 (1975).
- (8) R. G. Woolford, *Can. J. Chem.*, **40**, 1846 (1962).
- (9) D. M. Lichty, *Justus Liebigs Ann. Chem.*, **319**, 369 (1901).
- (10) C. A. Roian, *Ber.*, **54**, 3117 (1921).
- (11) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942).
- (12) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, N.Y., 1970, p 306.
- (13) C. S. Marvel and E. R. Birkhimer, *J. Am. Chem. Soc.*, **51**, 261 (1929).
- (14) A complete list of references is given by O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriguez, and R. Rucktschel, *J. Am. Chem. Soc.*, **94**, 1365 (1972). These authors report that a series of dialkyl-substituted α -lactones could be generated photochemically at very low temperature (77 K) and detected by IR spectroscopy.
- (15) G. Kortüm, W. Vogel, and K. Andrussow, IUPAC, "Dissociation Constants of Organic Acids in Aqueous Solutions", Butterworths, London, 1961.
- (16) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1969, p 10.
- (17) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 67 (1968); C. J. M. Stirling, *Angew. Chem., Int. Ed. Engl.*, **7**, 648 (1968); *J. Chem. Educ.*, **50**, 844 (1973).
- (18) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1973).
- (19) G. Illuminati, L. Mandolini, and B. Masci, *J. Am. Chem. Soc.*, **97**, 4960 (1975).
- (20) R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).
- (21) (a) As a general reference see J. Sicher, *Prog. Stereochem.*, **3**, 202 (1962); (b) see also Figure 2.
- (22) M. Sisido, *Macromolecules*, **4**, 737 (1971).
- (23) J. Dale, *J. Chem. Soc.*, 93 (1963).
- (24) L. Ruzicka, *Chem. Ind. (London)*, **54**, 2 (1935).
- (25) Reference 12, Chapter 12.

Unsaturated Carbenes from Primary Vinyl Triflates.

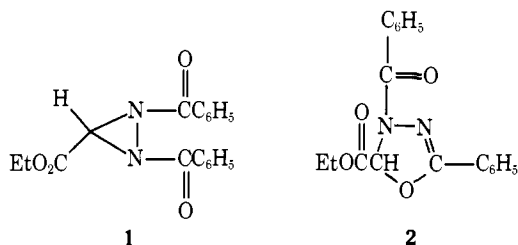
7. Reaction with Azoarenes^{1,2}

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Abstract: Reaction of triflate $(\text{CH}_3)_2\text{C}=\text{CHOTf}$ with azobenzene and *tert*-butylazobenzene in glyme with *t*-BuOK at -20°C gives 2-indazoles in good yield; no benzimidazoles were observed. The azobenzene adduct was identified by spectral means and oxidation to azobenzene-*o*-carboxylic acid. Reaction occurs via interaction of the triflate-derived carbene $(\text{CH}_3)_2\text{C}=\text{C}:$ with the azoarenes and represents a simple, single-step entry into this interesting class of 10- π -electron heterocyclic system.

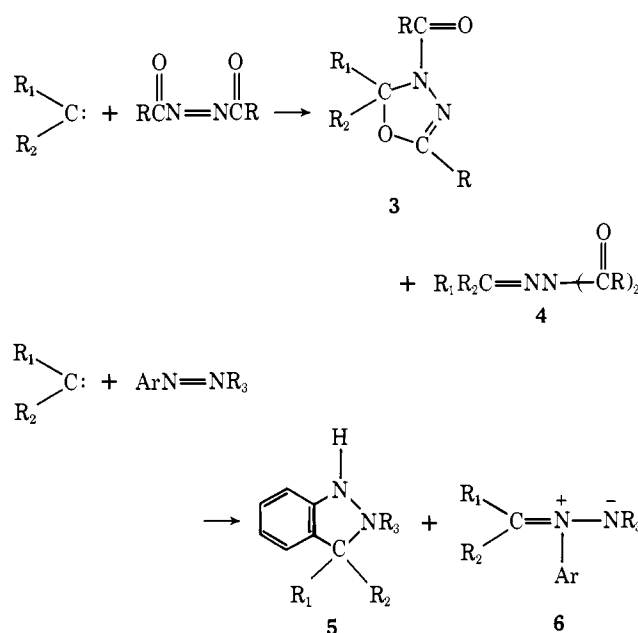
Carbenes readily add to olefins and alkynes to give cyclopropanes and cyclopropenes, respectively.³ Similarly, carbenes are known to interact with heteronuclear multiple bonds and particularly with $\text{C}=\text{N}$ and $\text{N}=\text{N}$ bonds.⁴ Reaction of carbenes with azo linkages is especially interesting for it can lead to novel heterocyclic compounds. The first such reaction was the interaction of carboethoxycarbene, derived from ethyl diazoacetate, with azodibenzoyl reported by Mueller⁵ to give diaziridine **1**, and for a number of years thereafter carbene



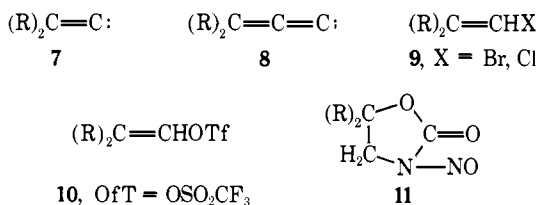
additions to azo compounds were interpreted in terms of such diaziridine adducts.⁶ It was not until the 1960's that Breslow⁷ and Fahr⁸ reexamined these reactions and showed that the actual product was not a diaziridine **1**, but an oxadiazoline **2**. In fact, interaction of carbenes with azo compounds generally falls in two categories, depending on the structure of the azo substrate, as shown in Scheme I. Azodicarbonyls (or azodicarboxylic esters) generally yield⁹ oxadiazolines **3** and/or hydrazones **4**, whereas azoarenes usually give¹⁰ dihydroindazoles, **5**, and/or azomethyne imines, **6**.

Recently besides normal carbenes there has been increasing interest in unsaturated carbenes,¹¹ **7** and **8**, generated by α elimination from vinyl halides,¹² **9**, or vinyl triflates,¹³ **10**, and base-promoted decomposition of *N*-nitrosooxazolidones,¹⁴ **11**.

Scheme I. Reaction of Carbenes with Carbonyl Azo Compounds and Azoarenes



These carbenes also readily interact with olefins¹¹ as well as alkynes,¹⁵ but little or no work has been done in the possible reaction of these species with heteronuclear multiple bonds and in particular azo compounds. There is but a single report,¹⁶ with no product identification, but only a 1:1 adduct claimed, on the interaction of an unsaturated carbene, **7**, with an azo compound, namely azobenzene, and a single report¹⁷ on the

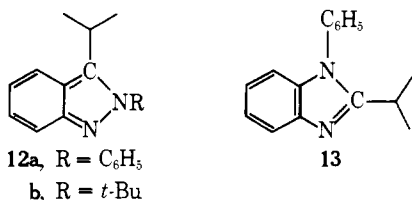


interaction of **8** ($\text{R} = \text{CH}_3$) also with azobenzene and also with scant product data.

The interaction of unsaturated carbenes **7** with azo linkages should be interesting both from a mechanistic as well as a synthetic point of view. Mechanistically, unsaturated carbenes, **7**, similar to normal carbenes, have been shown to be electrophilic¹⁸ and hence could interact with either the π system of $\text{N}=\text{N}$ bonds, analogous to their interaction with olefins resulting in alkylidenediaziridines, **14**, or with the nitrogen lone pair, resulting in a completely different pathway and product. Synthetically such unsaturated carbene additions to azo compounds could lead to novel routes into heterocyclic compounds or perhaps even new heterocyclics. Therefore, we undertook and report in this paper a detailed investigation into the reaction of the triflate-derived unsaturated carbene **7** with azoarenes.

Results and Discussion

Reaction of isopropylidencarbene (**7**, $\text{R} = \text{CH}_3$) derived from the primary vinyl triflate (**10**, $\text{R} = \text{CH}_3$) and *t*-BuOK with excess azobenzene in glyme at -20°C gave, after workup, a single crystalline product in 63% yield. Mass spectrum (vide infra) indicated the product to be a 1:1 adduct between the carbene and azobenzene and the proton NMR was consistent with either 2-phenyl-3-isopropylindazole, **12a**, or 1-phenyl-



2-isopropylbenzimidazole, **13**. The benzimidazole, **13**, could arise via initial addition of the carbene to the azo π system and formation of a alkylidenediaziridine, **14**, cleavage of the weak¹⁹ $\text{N}-\text{N}$ bond and subsequent rearrangement as shown in Scheme II, and analogous to the formation of a benzimidazole from the

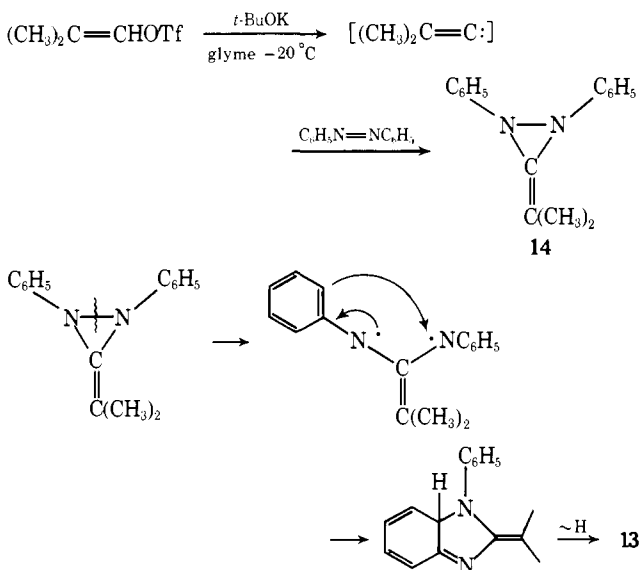


Table I. Comparison of the Prominent ^1H NMR, IR, and Mass Spectral Features of **12a** and **13**

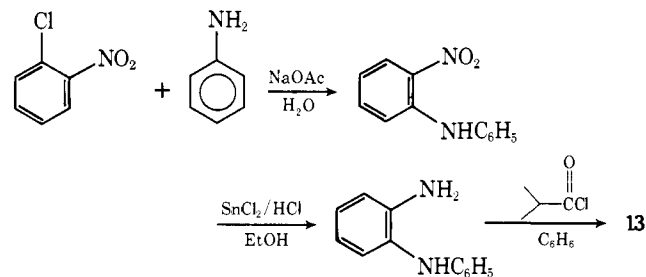
Spectral features	12a	13
^1H NMR (CCl_4 , int Me_4Si , δ)		
CH_3	1.44	1.42
CH	3.33	3.31
Aromatic H	7.42 and 6.4–7.9	6.8–7.8
IR, cm^{-1}		
$\text{C}=\text{C}$	1620	1597
$\text{C}=\text{N}$	1600	1515
Mass Spectrum		
M^+	236 (41%)	236 (67%)
Base peak	206	221

addition of **8** ($\text{R} = \text{CH}_3$) to azobenzene.¹⁷ The 2-indazole **12a** could arise via initial interaction of the carbene with the nitrogen lone pair and subsequent rearrangement (vide infra), analogous to the interaction of normal carbenes with azoarenes to give **5**.¹⁰ Hence there remained the problem of determining the exact structure of the product. This was accomplished by chemical as well as spectral means.

Although 2-indazoles²⁰ are a known²¹ class of heterocycles, to our knowledge compounds **12** are new and have not been previously reported. Furthermore, the standard methods of synthesis^{21a} of this class of compounds failed in our hands to give any **12**; therefore we decided to prepare by an independent means the better known benzimidazole **13**.

Synthesis of 13. The independent synthesis of 1-phenyl-2-isopropylbenzimidazole (**13**) was carried out by a modified literature procedure²² as shown in Scheme III. *o*-Aminodi-

Scheme III



phenylamine was prepared²³ from aniline and *o*-chloronitrobenzene as shown. Condensation of this *o*-aminodiphenylamine with isobutyryl chloride in refluxing benzene gave **13** in 70% yield. Physical as well as spectral properties (Table I) of authentic **13** clearly showed that 1-phenyl-2-isopropylbenzimidazole was *not* the same as the product obtained from the reaction of isopropylidencarbene with azobenzene. That left **12a** as the most likely structure for the product of the reaction of **7** ($\text{R} = \text{CH}_3$) with azobenzene.

Spectral Determinations. Product **12a** was fully characterized by means of its spectral properties and comparisons and contrasts of these properties with appropriate model compounds. A comparison of the prominent ^1H NMR, IR, and mass spectral features of **12a** and **13** is given in Table I. The UV features of **12a** and two model compounds, 2-methylindazole **15** and 1-methylbenzimidazole **16**, are given in Table II. The UV of **12a** is clearly more in line with that of 2-methylindazole **15** than that of 1-methylbenzimidazole **16**. Furthermore, the observed hypsochromic shift of 12 nm for **12a** at pH 1 is in line with equivalent shifts in related heterocycles.²⁴

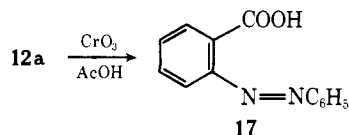
Finally the ^{13}C NMR of **12a** is given in Table III along with peak assignments. Once again the spectrum is not only com-

Table II. UV of **12a**, **15**, and **16**

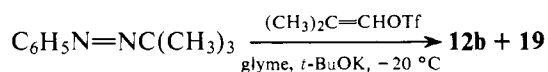
Compd	λ_{\max} (log ϵ)
12a (H ₂ O, pH 7.0)	279 (3.77), 303 (3.76)
12a (H ₂ O, pH 10.0)	277 (3.79), 302 (3.76)
12a (H ₂ O, pH 1.0)	266 (3.71), 300 (3.52)
15 (ref 24)	275 (3.80), 292 (3.79), 295 (3.78)
16 (ref 24)	249 (3.77), 254 (3.78), 266 (3.63), 274 (3.70), 281 (3.70)

pletely compatible with structure **12a**, but corresponds to the ¹³C spectra of similar indazoles.²⁵

Degradation of 12a. As final structure proof, adduct **12a** was oxidized²⁶ by means of CrO₃ in HOAc to the known²⁷ azobenzene-*o*-carboxylic acid **17**, whose physical and spectral properties were found identical with literature values.²⁷

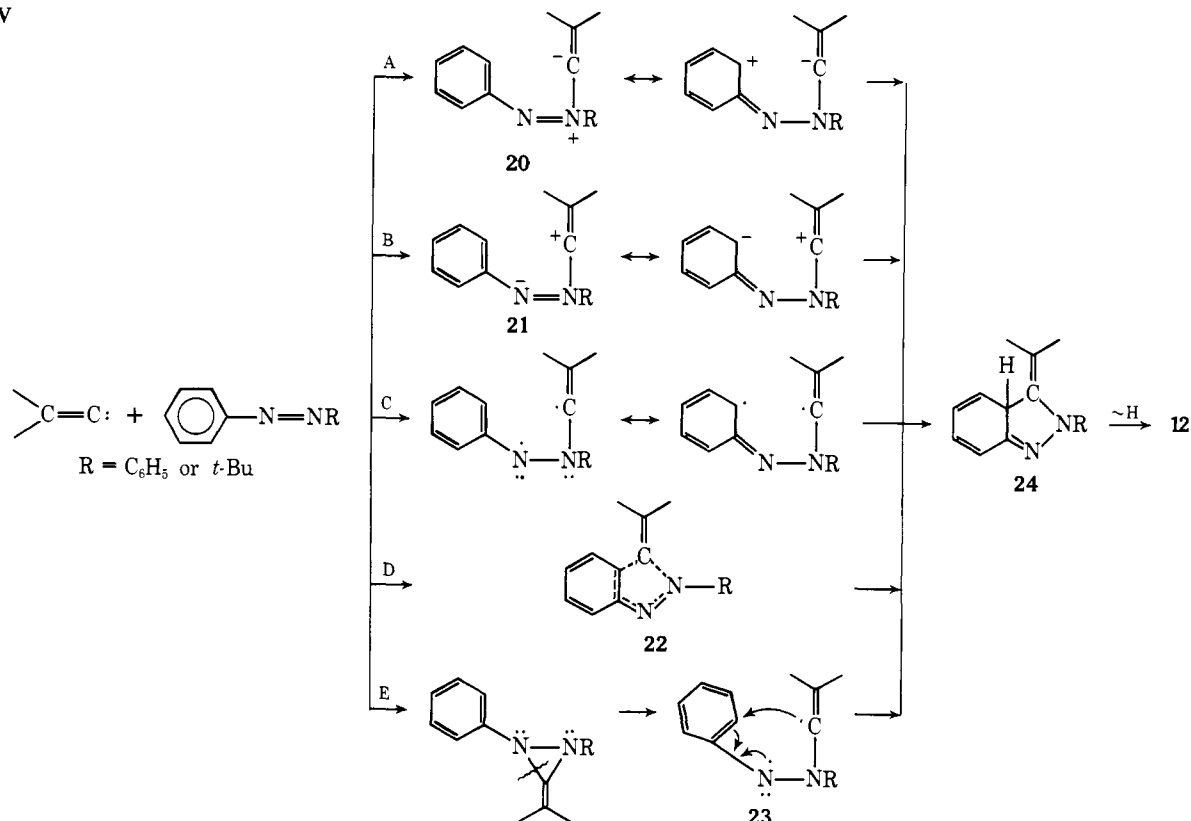


Addition of Isopropylidencarbene to *tert*-Butylazobenzene. To test the generality of such unsaturated carbene additions to azoarenes, isopropylidencarbene **7** (R = CH₃) was also reacted with *tert*-butylazobenzene, **18**. *tert*-Butylazobenzene was synthesized from *tert*-butyl chloride and C₆H₅N₂⁺BF₄⁻ by a procedure adapted from the literature.²⁸ This carbene addition gave product **12b** and a minor, incompletely identified product **19** that also corresponds to a 1:1 adduct (see Experimental Section).



Mechanistic Considerations. Although we have no direct evidence for any one mechanism for the formation of indazoles from the interaction of unsaturated carbenes **7** with azoarenes, a number of alternatives exist. Five possible mechanisms may be considered as outlined in Scheme IV. Paths A and B involve

Scheme IV

Table III. ¹³C Spectrum of **12a**

Carbon atom	Chemical shift, ppm from ref Me ₄ Si
C-1	148.9 (s) ^a
C-2	27.3 (d)
C-3	22.7 (q)
C-4	119.2 (s)
C-5, C-7	126.2 (d)
C-6	118.0 (d)
C-8	120.7 (d)
C-9	140.2 (s)
C-10	142.0 (s)
C-11=C-15	126.6 (d)
C-12=C-14	129.2 (d)
C-13	121.2 (d)

^a Multiplicity of (H)-undecoupled peak; s = singlet; d = doublet; q = quartet.

interaction of the carbene with the nitrogen lone pair and formation of zwitterionic ylide-type intermediates **20** and **21** that can ring close to **24** and upon hydrogen shift²⁹ result in the observed product. Path A involves electrophilic attack and initial interaction with the empty p-orbital, whereas path B involves nucleophilic behavior on the part of the carbene and initial interaction with the carbenoid pair of electrons. Since unsaturated carbenes, **7**, have been shown to be electrophilic,¹⁸ at least toward olefins, and since most normal carbenes show electrophilic behavior³ as well, path A seems much more likely. Such zwitterionic intermediates are well preceded in the literature³⁰ and have been suggested as intermediates in normal carbene additions to certain azo compounds.^{9,10} Route C involves a biradicaloid mechanism, implying a radical character

and behavior for carbene **7**. Since there is no precedent for singlet carbenes acting as radicals,³ and since **7** has been shown to be a singlet,³¹ this mechanism seems unlikely. Path D involves a concerted 1,4-cheletropic addition of the singlet carbene to azobenzene via **22**. This thermal 1,4-addition, although symmetry allowed by the Woodward-Hoffmann rules,³² is discriminated against by closed-shell repulsive interactions.³³ Indeed there are very few bona fide examples of 1,4-carbene additions known.³⁴ However, it has been shown that although a 1,2-addition for most carbenes is favored over a 1,4-addition for most 1,3-dienes, a shift toward 1,4-addition is predicted with the incorporation of electron-withdrawing substituents on the dienes. Hence, replacement of some of the diene carbons by more electronegative atoms, such as nitrogen in azo linkages or oxygen in carbonyls and others, perhaps shifts electron density sufficiently to cause 1,4-addition to occur. Indeed F₂C: has been shown to undergo 1,4-addition to a steroidal cisoid enone.³⁵ Finally, path E involves carbene addition to the N=N π system, alkylidenediaziridine formation as in Scheme II, but breakage of the C-N instead of N-N bond to give **23**, and subsequent rearrangement analogous to Scheme II to form **24**, followed by **12**.²⁹ However, since C-N bonds are considerably stronger than N-N bonds¹⁹ (about 70 vs. 38 kcal/mol)³⁶ such a path in preference to N-N cleavage and benzimidazole formation (Scheme II) is very unlikely. Since no benzimidazole was observed in these reactions this effectively rules out mechanism D. In our judgement path A, interaction of the carbene with the nitrogen lone pair to form ylide **20** and its subsequent reactions, analogous to the behavior¹⁰ of normal carbenes as shown in Scheme I, is most likely.

In summary, we have shown that unsaturated carbenes, **7**, readily interact with azoarenes to give 1:1 adducts in good yields. These adducts were shown by spectral and chemical means to be 2-indazoles. The most likely mechanism involves interaction of the carbene with the nitrogen lone pair and formation of ylide **20**, which upon ring closure and hydrogen migration gives the observed product **12**. Such unsaturated carbene addition to azoarenes represents a simple, single-step entry into this interesting class of 10- π -electron heterocyclic systems.

Experimental Section

General. All boiling and melting points are uncorrected. Melting points were taken on a Thomas-Hoover melting point apparatus. Infrared spectra were recorded on a Beckman IR5A and are reported in wavenumbers (cm⁻¹) calibrated to the 1602-cm⁻¹ line of polystyrene. UV were recorded on a Cary-17, and proton NMR on a Varian A-60 spectrometer. Carbon-13 NMR spectra were run on a Varian XL-100 spectrometer operating in the Fourier transform mode locked on CDCl₃. Mass spectra were recorded on a AEI-MS-30 spectrometer. Preparative GC was carried out on a Varian-Aerograph 90P chromatograph.

Addition of Isopropylidene carbene to Azobenzene, Formation of 12a. Into a 200-mL round-bottom flask equipped with a magnetic stirring bar and a stopper were added 2.46 g (22 mmol) of sublimed *t*-BuOK and 20 g (120 mmol) of freshly recrystallized azobenzene (Eastman Kodak) followed by 150 mL of anhydrous 1,2-dimethoxyethane. The mixture was cooled to -20 °C, then 4.08 g (20 mmol) of (CH₃)₂C=CHOSO₂CF₃ was added in four portions over a 20-min period. The reaction mixture was stirred at -20 °C for 48 h, then the solvent was evaporated on a rotary evaporator and the residue dissolved in 200 mL of ether. The ether solution was extracted with four 25-mL portions of 0.1 N HCl and the combined aqueous layer back extracted with two 25-mL portions of ether. After drying the combined organic layer over MgSO₄ the ether was evaporated on a rotary evaporator and the crude product recrystallized from ethanol-water resulting in 3.0 g (63%) of product **12a**: mp 83-84 °C; NMR (CCl₄, int Me₄Si) δ 1.44 (d, *J* = 7.0 Hz, 6 H, CH₃), 3.33 (septet, *J* = 7.0 Hz, 1 H, CH), 7.42 (s, ~5 H, C₆H₄), 6.4-7.9 (m, 4 H, C₆H₄); IR (Nujol

mull) 1620, 1600, 1503, 1458, and 1230 cm⁻¹; UV (CH₃OH) 278 nm (log ϵ 3.77) and 303 nm (log ϵ 3.75); mass spectrum 236 (M⁺, 41), 222 (39), 221 (93), 220 (28), 219 (62), 206 (100), 205 (53), 195 (25), 167 (55), 118 (26), 115 (55), 103 (47), 91 (37), 77 (45), 51 (68); ¹³C NMR (CDCl₃, ppm rel to Me₄Si) as reported in Table III.

Preparation of Authentic Benzimidazole 13. Into a 250-mL three-necked round-bottom flask, equipped with a magnetic stirring bar, reflux condenser, and an addition funnel, was added 9.2 g (0.05 mol) of *o*-aminodiphenylamine (prepared²³ as shown in Scheme III) and 100 mL of dry benzene. To the stirred solution was slowly added over a period of 1 h 6.4 g (0.06 mol) of isobutryl chloride. After addition was complete the mixture was refluxed for 4 h, then cooled. During refluxing a reddish-brown precipitate formed. The cold reaction mixture was neutralized with dilute NaOH then washed several times with water and dried over MgSO₄. After evaporation of the benzene on a rotary evaporator the residue was recrystallized from chloroform-pentane to give 8.2 g (70%) of product **13**: mp 61-63 °C; NMR (CCl₄, int Me₄Si) δ 1.42 (d, *J* = 7.0 Hz, 6 H, CH₃), 3.31 (septet, *J* = 7.0 Hz, 1 H, CH), 6.8-7.8 (m, 9 H, C₆H₅ and C₆H₄); IR (film) 1597, 1515, 1433, and 1214 cm⁻¹; mass spectrum 236 (M⁺, 67), 235 (33), 222 (19), 221 (100), 219 (14), 206 (19), 167 (10), 145 (40), 132 (24), 105 (13), 77 (16), 51 (13).

Oxidation of 12a to 17. Into a 100-mL round-bottom flask, equipped with a magnetic stirring bar and reflux condenser, was added 3.02 g (12.8 mmol) of **12a** from the above reaction along with 30 mL of acetic acid followed by 6.4 g (64 mmol) of chromic anhydride. The reaction mixture was stirred and refluxed for 24 h, then cooled and extracted with four 50-mL portions of ether. The combined ether layer was washed with two 50-mL portions of H₂O then dried over MgSO₄. After filtration and evaporation of the ether the dark residue was triple-sublimed at 90 °C (10⁻³ Torr) to give 1.64 g (57%) of yellow-orange solid **17**: mp 93-94 °C (lit.²⁷ 94.5 °C); NMR (CDCl₃, int Me₄Si) δ 7.4-8.5 (m, 9 H, C₆H₅ and C₆H₄), 12.0 (br s, 1 H, COOH); IR (Nujol mull) 3279 (OH), 1715 (C=O), 1449, 1277, 1225, 776, and 682 cm⁻¹; mass spectrum 226 (M⁺, 38), 181 (12), 153 (10), 152 (12), 149 (10), 121 (24), 105 (55), 93 (16), 78 (10), 77 (100), 65 (16), 52 (19).

Preparation of *tert*-Butylazobenzene (18). This compound was prepared by an adaptation of the procedure of Curtin and Ursprung.²⁸ A solution of *tert*-butylmagnesium chloride was prepared from 14.6 g (0.6 mol) of magnesium turnings and 50.9 g (0.55 mol) of *tert*-butyl chloride in 500 mL of ether, then forced with N₂ pressure into a 2-L round-bottom flask containing 82 g (0.5 mmol) of freshly fused anhydrous zinc chloride in 750 mL of anhydrous ether. A copious white precipitate of *tert*-butylzinc chloride formed and after 1 h the reaction mixture was vigorously shaken and the *entire* mixture slowly forced with N₂ pressure into a 3-L flask containing a cooled (ice-salt bath) suspension of 96 g (0.5 mol) of benzenediazonium fluoroborate in 600 mL of anhydrous ether. After addition was complete, the mixture was stirred at room temperature for 24 h, then decomposed with 250 mL of saturated NH₄Cl solution. The mixture was extracted with several portions of water and the aqueous layer back-extracted with ether. The ether was evaporated and the crude product was steam-distilled to give a yellow oil, which was vacuum distilled to give 29.4 g (48%) of *tert*-butylazobenzene (**18**): bp 59-64 °C (0.25 mm); NMR (neat, int Me₄Si) δ 1.34 (s, 9 H), 7.21-7.78 (m, 5 H, C₆H₅); IR (neat) 1590, 1475, 1451, 1359, 762, and 689 cm⁻¹.

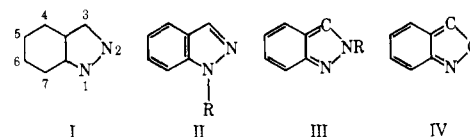
Addition of Isopropylidene carbene to 18, Formation of 12b. Into a 25-mL round-bottom flask, equipped with a magnetic stirring bar and a stopper, was added 0.67 g (6 mmol) of sublimed *t*-BuOK and 15 mL of *tert*-butylazobenzene (**18**). The mixture was cooled to -20 °C, then 1.02 g (5.0 mmol) of (CH₃)₂C=CHOSO₂CF₃ was added and the reaction stirred for 48 h at -20 °C. The mixture was diluted with 50 mL of pentane and extracted with water. The organic layer was dried over MgSO₄ and after filtration the pentane and *tert*-butylazobenzene were distilled off. The residue was analyzed by GC and found to contain two products in a ratio of 80:20. The two products were isolated by preparative GC on a 5 ft \times 0.25 in. 10% SF-96 on 60-80 Chrom W column. The major product was **12b**: NMR (CCl₄, int Me₄Si) δ 1.43 (d, *J* = 7.0 Hz, 6 H, CH₃), 1.67 (s, 9 H), 3.67 (septet, *J* = 7.0 Hz, 1 H, CH), 6.6-7.7 (m, 4 H, C₆H₄); IR (neat) 1610, 1477, 1241, and 1208 cm⁻¹; mass spectrum 216 (M⁺, 45), 201 (8), 160 (100), 146 (29), 145 (84), 132 (8), 119 (14), 115 (7), 92 (14), 91 (7). For minor product **19**:³⁷ NMR (CCl₄, int Me₄Si) δ 1.6 (s, 9 H), 2.03 (s, 3 H, CH₃), 5.06 (br s, 1 H), 5.37 (br s, 1 H), 6.6-7.7 (m, 4 H, C₆H₅); IR (neat) 1639, 1616, 1468, 1255, and 1205 cm⁻¹; mass

spectrum, 214 (M^+ , 91) 159 (56), 158 (100), 157 (87), 143 (22), 131 (22), 130 (26), 129 (23), 128 (18), 118 (35), 115 (30).

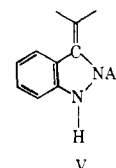
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References and Notes

- (1) Paper 6: P. J. Stang, J. R. Madsen, M. G. Mangum, and D. P. Fox, *J. Org. Chem.*, in press.
- (2) Abstracted in part from the Ph.D. Thesis of M. G. Mangum, The University of Utah, 1975.
- (3) For reviews and leading references see: (a) M. Jones Jr., and R. A. Moss, "Carbenes", Vol. I, Wiley, New York, N.Y., 1973; (b) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971.
- (4) For leading references see: A. P. Marchand in "The Chemistry of Functional Groups: Supplementary Volume 1", S. Patai, Ed., Wiley-Interscience, London, in press.
- (5) E. Mueller, *Ber.*, **47**, 3001 (1914).
- (6) R. A. Reed, *Chem. Ind. (London)*, 529 (1966).
- (7) R. Breslow, C. Yaroslavsky, and S. Yaroslavsky, *Chem. Ind. (London)*, 1961 (1961).
- (8) E. Fahr, *Angew. Chem.*, **73**, 536 (1961).
- (9) E. Fahr, K. Königsdorfer, and F. Schekenbach, *Justus Liebigs Ann. Chem.*, **690**, 138 (1965); E. Fahr, K. H. Keil, H. Lind, and F. Schekenbach, *Z. Naturforsch., B*, **20**, 526 (1965); G. F. Bettinetti and L. Capretti, *Gazz. Chim. Ital.*, **95**, 33 (1965); E. Fahr, K. Doppert, K. Königsdorfer, and F. Schekenbach, *Tetrahedron*, **24**, 1011 (1968); D. Seyferth and H. Shih, *J. Org. Chem.*, **39**, 2329, 2336 (1974).
- (10) J. Markert and E. Fahr, *Tetrahedron Lett.*, 4337 (1967); M. Colonna, P. Bruni, and G. Guerra, *Gazz. Chim. Ital.*, **97**, 1052 (1967); E. Fahr, J. Markert, and N. Peiz, *Justus Liebigs Ann. Chem.*, 2088 (1973); D. Seyferth, W. Tronich, and H. Shih, *J. Org. Chem.*, **39**, 158 (1974).
- (11) For a general review and leading references see: H. D. Hartzler in "Carbenes", Vol. II, R. A. Moss and M. Jones Jr., Ed., Wiley, New York, N. Y., 1975.
- (12) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).
- (13) P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562 (1974).
- (14) M. S. Newman et al., *J. Am. Chem. Soc.*, **90**, 4189 (1968); **91**, 6461 (1969); **92**, 4312 (1970); *J. Org. Chem.*, **34**, 1220 (1969); **38**, 547 (1973).
- (15) P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **97**, 3854 (1975); M. S. Newman and C. D. Beard, *J. Org. Chem.*, **35**, 2412 (1970).
- (16) Y. N. Kuo and M. J. Nye, *Can. J. Chem.*, **51**, 1995 (1973).
- (17) T. Sasaki, S. Eugichi, and T. Ogawa, *Heterocycles*, **3**, 193 (1975).
- (18) (a) P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **97**, 6478 (1975); (b) T. B. Patrick, E. C. Hagnie, and W. J. Probst, *J. Org. Chem.*, **37**, 1553 (1972); (c) M. S. Newman and T. B. Patrick, *J. Am. Chem. Soc.*, **91**, 6461 (1969).
- (19) K. Tarama, "Handbook of Organic Structural Analysis", Y. Yukawa, Ed., W. A. Benjamin, New York, N.Y., 1965; T. L. Cottrell, "The Strength of Chemical Bonds", Butterworth, London, 1954.
- (20) The indazoloid ring system,^{21a} I, has two members 1-indazole, II, and 2-indazole, III, depending on which nitrogen bears the substituent; 2-indazoles have also occasionally been referred to as azaanthranils, due to their similarity to anthranils, IV.



- (21) (a) L. C. Behr in "Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles, and Condensed Rings", R. H. Wiley, Ed., Interscience, New York, N.Y., 1967, pp 289-382; (b) R. C. Elderfield, *Heterocycl. Compd.*, **5**, 162-193 (1957).
- (22) M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).
- (23) F. Kehrman and E. Havas, *Ber.*, **46**, 342 (1913).
- (24) A. R. Katritzky, *Phys. Methods Heterocycl. Chem.*, **3**, 97 (1971).
- (25) R. G. Rees and M. J. Green, *J. Chem. Soc. B*, 387 (1968).
- (26) C. Paal, *Ber.*, **24**, 3058 (1891).
- (27) C. P. Joshua and G. E. Lewis, *Aust. J. Chem.*, **20**, 929 (1967).
- (28) D. Y. Curtin and J. U. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956).
- (29) This hydrogen shift can occur one of two ways: (a) some sort of 1,3 shift to C and formation of the observed product **12a**; or (b) an initial shift to N to give V, followed by a second shift to C to give **12a**.



- (30) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963); *J. Org. Chem.*, **41**, 403 (1976).
- (31) P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **97**, 1459 (1975).
- (32) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Springer-Verlag, Berlin, and Academic Press, New York, N.Y., 1970, and references cited therein; (b) T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry", Cambridge University Press, Cambridge, 1972.
- (33) H. Fujimoto and R. Hoffmann, *J. Phys. Chem.*, **78**, 1167 (1974).
- (34) M. Jones Jr., W. Ando, M. E. Hendrick, A. Kulczycki Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Am. Chem. Soc.*, **94**, 7469 (1972).
- (35) P. Hodge, J. A. Edwards, and J. H. Fried, *Tetrahedron Lett.*, 5175 (1966).
- (36) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966, p 100.
- (37) These spectral data are consistent with, but do not prove a structure such as VI for **19**.

