(ca. 25 mL) and stirred under a nitrogen atmosphere for 16 h at room temperature. The dark color of iodine develops almost immediately and iodine crystallizes from the solution as the reaction progresses. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of a saturated solution of sodium thiosulfate. The mixture was extracted with methylene chloride  $(2 \times 50 \text{ mL})$ . The extracts were

dried over anhydrous magnesium sulfate and the solvent was removed to yield a crude product which was taken up in hexane and filtered through a short silica gel column. Removal of the solvent afforded p-tolyl disulfide (1.1 g, 89%), mp 46.0 °C (lit.  $^{12}$ mp 48 °C).

Procedure for Conversion of p-Toluenesulfonyl Chloride to p-Tolyl Disulfide with Chlorotrimethylsilane/Sodium Iodide. Chlorotrimethylsilane (7.6 g, 70 mmol) was added to a stirred solution of p-toluenesulfonyl chloride (1.9 g, 10 mmol) in dry acetonitrile (30 mL). Sodium iodide (12 g, oven dried) was added and the mixture was stirred for 16 h at room temperature under a nitrogen atmosphere. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of sodium thiosulfate. The mixture was extracted with ether  $(3 \times 25 \text{ mL})$  and the combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent afforded p-tolyl disulfide (0.96 g, 79%), mp 46.0 <sup>o</sup>C (lit.<sup>12</sup> mp 48 °C).

Procedure for Conversion of *p*-Bromobenzenesulfonyl Chloride to p-Bromophenyl Disulfide with Hexamethyldisilane/Iodine. Iodine (0.25 g, 1.0 mmol) was added to a stirred solution of p-bromobenzenesulfonyl chloride (1 g, 4 mmol) and hexamethyldisilane (1.75 g, 12.0 mmol) in methylene chloride (ca. 25 mL) and the mixture was stirred for 16 h at room temperature. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of sodium thiosulfate. The mixture was extracted with methylene chloride  $(3 \times 25 \text{ mL})$ and the extracts were dried over anhydrous magnesium sulfate. The solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent gave p-bromophenyl disulfide (0.59 g, 80%), mp 95.2 °C (lit.<sup>12</sup> mp 94.5 °C).

Procedure for Conversion of *p*-Chlorobenzenesulfonyl Chloride to p-Chlorophenyl Disulfide with Chlorotrimethylsilane/Sodium Iodide under Phase-Transfer Conditions. Sodium iodide (15 g, 100 mmol) was suspended in a solution of chlorotrimethylsilane (5.5 g, 50 mmol) in methylene chloride (ca. 50 mL) containing a catalytic amount of tetra-nbutylammonium iodide (200 mg). p-Chlorobenzenesulfonyl chloride (2.1 g, 10 mmol) was added and the mixture was stirred for 16 h at room temperature. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of a saturated solution of sodium thiosulfate. The mixture was extracted with methylene chloride  $(2 \times 50 \text{ mL})$ . The extracts were dried over anhydrous magnesium sulfate and the solvent was removed to yield a crude product which was taken up in hexane and filtered through a short column of silica gel. Removal of the solvent afforded *p*-chlorophenyl disulfide (1.4 g, 97%), mp 70.0 °C (lit.<sup>12</sup> mp 73 °C).

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Registry No. Iodotrimethylsilane, 16029-98-4; CH<sub>3</sub>SO<sub>2</sub>Cl, 124-63-0; CH<sub>3</sub>CH<sub>2</sub>SO<sub>2</sub>Cl, 594-44-5; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SO<sub>2</sub>Cl, 1939-99-7; C<sub>6</sub>H<sub>5</sub>S- $\begin{array}{l} O_2Cl, \ 98-09-9; \ p-CH_3C_6H_4SO_2Cl, \ 98-59-9; \ p-CH_3C_6H_4SO_2Br, \ 1950-69-2; \\ p-BrC_6H_4SO_2Cl, \ 98-58-8; \ p-ClC_6H_4SO_2Cl, \ 98-60-2; \\ p-FC_6H_4SO_2Cl, \ 349-88-2; \ p-FC_6H_4SOCl, \ 50986-83-9; \\ p-FC_6H_4SO_2Cl, \ 349-88-2; \\ p-FC_6H_4SO_2Cl, \ 50986-83-9; \\ p-FC_6H_4SO_2C$ 1535-35-9; p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Na, 824-79-3; p-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Me, 455-15-2; CH<sub>3</sub>SSCH<sub>3</sub>, 624-92-0; CH<sub>3</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>3</sub>, 110-81-6; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SSC- $\begin{array}{l} H_2C_6H_5, 150\text{-}60\text{-}7; \ C_6H_5SSC_6H_5, 882\text{-}33\text{-}7; \ p\text{-}CH_3C_6H_4SSC_6H_4CH_3\text{-}p, \\ 103\text{-}19\text{-}5; \ p\text{-}BrC_6H_4SSC_6H_4Br\text{-}p, \ 5335\text{-}84\text{-}2; \ p\text{-}ClC_6H_4SSC_6H_4Cl\text{-}p, \end{array}$ 1142-19-4; p-FC<sub>6</sub>H<sub>4</sub>SSC<sub>6</sub>H<sub>4</sub>F-p, 405-31-2.

## **Base-Assisted "Carbon-Claisen" Rearrangement of** 4-Phenyl-1-butene

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The [3,3] sigmatropic rearrangements of all carbon systems in which one unsaturated site is constrained within an aromatic ring are poorly understood despite the fact that such rearrangements are related to both the Cope and Claisen rearrangements. No conversion of 4-phenyl-1butene (1) to 3-(o-tolyl)propene (2) was observed in the



thermolysis of 1 in a flow system at 400 °C and above<sup>1</sup> or in sealed tubes at 400 °C.<sup>2</sup> Similarly, various 4-aryl-1butenes, some embellished with substituents known to facilitate Cope rearrangements, gave upon thermolysis only traces of materials which could have arisen from [3,3] sigmatropic rearrangements.<sup>2,3</sup> In contrast, 1 has been reported to give a high yield of a mixture of o-tolylpropenes when heated at 350 °C in the presence of potassium *tert*-butoxide.<sup>4</sup> Thus, it was postulated that the first step in the conversion of 1 to 2, the sigmatropic rearrangement, was reversible and occurred readily at 350 °C, but the second step, isomerization of the intermediate to 2, was slow. The added base served as a catalyst for the second step.<sup>5</sup> Recently, however, elegant deuterium-labeling studies by Lambert, Fabricius, and Napoli have shown that the [3,3] sigmatropic rearrangement step for a 4-aryl-1butene must be a high-energy process.<sup>9</sup> Taken together, these results suggest an unusual role for the base in the reported conversion of 1 to 2 and its isomers. With the intention of characterizing this base effect, we planned a <sup>13</sup>C isotope labeling study, but we have found, contrary to the previous report, that 1 is not converted to o-tolylpropenes upon thermolysis in the presence of potassium tert-butoxide.

Eight  $C_{10}H_{12}$  isomers (five phenylbutenes and three o-tolylpropenes) might be detected in the reaction mixtures after thermolysis of 1 in the presence of potassium tertbutoxide. We were able to resolve all eight isomers by gas chromatography on an XF-1150 column and, thus, could analyze products directly. Compound 2 was not completely resolved from (E)-1-phenyl-2-butene and (Z)-1-phenyl-1butene and could not have been detected by our technique if present in small amounts (<5%). However, the predominant o-tolylpropene present after a base-catalyzed equilibration of 2 is (E)-1-(o-tolyl)propene which was

(9) Lambert, J. B.; Fabricius, D. M.; Napoli, J. J. J. Am. Chem. Soc. 1979, 101, 1793-1800.

0022-3263/80/1945-4793\$01.00/0 © 1980 American Chemical Society

<sup>(12)</sup> Reid, E. E. "The Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Company Inc.: New York, 1960.

Hurd, C. D.; Bollman, H. T. J. Am. Chem. Soc. 1934, 56, 447-449.
 Lambert, J. B.; Fabricius, D. M.; Hoard, J. A. J. Org. Chem. 1979, 44, 1480-1485.

 <sup>(3) (</sup>a) Cope, A. C.; Field, L.; MacDowell, D. W. H.; Wright, M. E. J.
 Am. Chem. Soc. 1956, 78, 2547-2551. (b) Cope, A. C.; Meili, J. E.;
 MacDowell, D. W. H. Ibid. 1956, 78, 2551-2556.
 (4) Doering, W. von E.; Bragole, R. A. Tetrahedron 1966, 22, 385-391.

<sup>(5)</sup> Two carbon-Claisen rearrangements which could be activated by cyclopropyl bond cleavage<sup>6,7</sup> and one such rearrangement in a relatively unactivated system<sup>8</sup> have been reported.

 <sup>(6)</sup> Marvell, E. N.; Lin, C. J. Am. Chem. Soc. 1978, 100, 877–883.
 (7) Maas, G.; Regitz, M. Angew. Chem., Int. Ed. Engl. 1977, 16, 711 - 712

<sup>(8)</sup> Yasuda, M.; Harano, K.; Kanematsu, K. J. Org. Chem. 1980, 45. 2368-2372

cleanly resolved by our analytical technique and could readily be detected in <1% relative yield.

As reported previously,<sup>4</sup> base-catalyzed isomerization of 1 under relatively mild conditions gave a mixture of the five phenylbutenes in which (E)-1-phenyl-1-butene predominated. Similarly, mild base-catalyzed isomerization of 2 gave a mixture of 2 and (Z)- and (E)-1-(o-tolyl)propene; at 70 °C the equilibrated mixture contained these three products in 0.1, 8, and 92%, respectively.

Several thermolyses of 1 under the conditions reported<sup>4,10</sup> to give 2 and its isomers were conducted; in no case did we observe significant amounts of *o*-tolylpropenes. Various modifications of the reported thermolysis conditions (including altering the ratios of the reagents, the reaction temperature, and the reaction time) were made. Again no significant amounts of *o*-tolylpropenes were detected, although a trace (<0.3% relative yield) of a compound with a GC retention time similar to that of (*E*)-1-(*o*-tolyl)propene was formed in some reactions. At temperatures above 350 °C, substantial decomposition of the phenylbutenes to form predominantly lower weight products occurred as previously reported.<sup>1,2</sup>

We cannot readily rationalize the source of error in the original study; however, we did observe that the 350 °C base-catalyzed isomerization of 1 to other phenylbutenes occurred with about the same rate as the reported conversion of 1 to o-tolylpropenes.<sup>10</sup> Since (E)-1-phenyl-1butene and (E)-1-(o-tolyl)propene have virtually identical retention times on several GC columns, one can envision preliminary studies in which GC peaks were misassigned. The reported<sup>4,10</sup> isolation of methyl o-toluate upon potassium permanganate oxidation and diazomethane treatment of the product mixtures cannot be explained. When we submitted a mixture of phenylbutenes to potassium permanganate oxidation, we obtained only benzoic acid as determined by <sup>1</sup>H NMR spectroscopy of the acidic products; this reaction was peformed half a century ago with the same results.<sup>1</sup>

The reported conversion of 1 to o-tolylpropenes has been cited as a precedent in mechanistic interpretations of related possible "carbon-Claisen" rearrangements;<sup>5</sup> however, our results support Lambert's conclusion<sup>9</sup> that a [3,3] signatropic rearrangement step in the all-carbon analogue of the Claisen rearrangement must be a high energy process. In possible "carbon-Claisen" rearrangements not activated by a cyclopropyl bond rupture,<sup>8</sup> we suggest that alternative mechanisms not involving [3,3] sigmatropic shifts should be considered.

## **Experimental Section**

4-Phenyl-1-butene (1) was prepared in 83% yield from the reaction of 40 mequiv of allylmagnesium chloride with 5 g (30 mmol) of benzyl bromide [bp 175–180 °C (lit.<sup>11</sup> bp 175–178 °C)].

**3-(o-Tolyl)propene** (2) was prepared in 58% yield from the reaction of 90 mequiv of *o*-tolylmagnesium bromide and 8 g (100 mmol) of freshly distilled allyl chloride according to the method of Doering and Bragole<sup>4</sup> [bp 112 °C (50 torr) (lit.<sup>1</sup> bp 93–95 °C (30 torr))].

Thermolyses of 1 (100–200  $\mu$ L) in the same volume of 0.4 M potassium *tert*-butoxide in *tert*-butyl alcohol with a trace of hydroquinone were conducted as described by Doering and Bragole.<sup>4,10</sup> A gas chromatograph oven was as the thermolysis chamber. Temperatures were measured with a copper–constantan thermocouple and are believed to accurate to ±5 °C. After the thermolyses, the reaction tubes were allowed to cool to room temperature. The reaction tubes were cooled to -78 °C and broken

open. The reaction mixtures were diluted with ether, washed with water, 1% aqueous HCl solution, and saturated aqueous NaCl solution, and dried  $(MgSO_4)$ . The product mixtures were analyzed by gas chromatography on a 1/8 in. by 15 ft column containing 3% XF-1150 on 80/100 Chromosorb G (non acid washed). Under our conditions the eight  $C_{10}H_{12}$  isomers of interest eluted in the following order: compound (relative retention time), (Z)-1-(otolyl)propene (0.50), 4-phenyl-1-butene (1) (0.53), (E)-1phenyl-2-butene (0.56), 3-(o-tolyl)propene (2) (0.59), (Z)-1phenyl-1-butene (0.62), (Z)-1-phenyl-2-butene (0.68), (E)-1-(otolyl)propene (0.94), (E)-1-phenyl-1-butene (1.00). In several thermolyses run at 350 °C for 8 to 17 h, the major product was (E)-1-phenyl-1-butene (44-68%), and in each case <5% 3-(otolyl) propene and <1% (E)-1-(o-tolyl) propene were present. The modified thermolyses included reactions run at 330 °C (9 h) and 370 °C (12 h), reactions run without hydroquinone, and reactions run without tert-butyl alcohol at temperatures from 330-370 °C.

The reactions described below were run under nitrogen; transfers of solutions were made by syringe.

1-Phenyl-1-butenes. Sodium hydride (2.4 g of a 50% suspension in oil, 50 mmol) in a 200-mL flask was washed with 20 mL of dry pentane. Dimethyl sulfoxide (Me<sub>2</sub>SO) (25 mL, distilled from calcium hydride) was added to the reaction flask, and the resulting mixture was heated with stirring in a 70 °C oil bath for 1 h. After the mixture was cooled to 0 °C, 21.6 g (50 mmol) of triphenylpropylphosphonium iodide in 50 mL of Me<sub>2</sub>SO (partial suspension) was added. The reaction mixture was allowed to warm to room temperature and then was again cooled to 0 °C. Benzaldehyde (5.8 g, 55 mmol) was added dropwise, and the resulting mixture was warmed to room temperature and then stirred for 2 h. The mixture was poured into 150 mL of water, and the resulting mixture was extracted with ether  $(3 \times 50 \text{ mL})$ . The combined ethereal washes were filtered to remove triphenylphosphine oxide, washed with 50 mL of saturated aqueous NaCl solution, and dried  $(MgSO_4)$ . The mixture was filtered, and the ether was distilled through a 6-in. fractionating column. The residue was distilled to give 5.52 g (42 mmol, 84%) of a mixture of (Z)- and (E)-1-phenyl-1-but enes, bp 132–137 °C (95 torr) (lit.<sup>12</sup> bp 187 °C (Z) and 199 °C (E)). GC analysis ( $^{1}/_{8}$  in. × 15 ft, 3% XF-1150 on Chromosorb G, 110 °C) showed two components with a relative area ratio of 65:35 for the peaks with retentions of 10.5 (Z) and 17.0 (E) min, respectively. Preparative GC  $(^3/_8 \text{ in.} \times 14)$ ft, 20% Apiezon L on 60/80 Chromosorb A, 190 °C) permitted purification of the Z and E isomers which, upon analytical GC, were shown to be 99% and 96% pure, respectively. For (Z)-1phenyl-1-butene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.0 (t, 3 H, J = 7.5 Hz), 2.3 (m, 2 H), 5.6 (m, 1 H), 6.4 (m, 1 H), 7.3 (s, 5 H). For (Z)-1phenyl-1-butene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.1 (t, 3 H, J = 7.5 Hz), 2.2 (m, 2 H), 5.8-6.7 (complex m, 2 H), 7.2 (s, 5 H).

1-(o-Tolyl)propenes were prepared by a Wittig reaction similar to that described above, employing the Wittig reagent prepared from 21 g (50 mmol) of triphenylethylphosphonium iodide and 6.0 g (50 mmol) of o-tolualdehyde. Distillation gave 4.5 g (34 mmol, 68%) of a mixture of isomers, bp 130-135 °C (90 torr) (lit.<sup>13</sup> bp 188-190 °C). Analytical GC (XF-1150) showed two components: (Z) 35%, 8.5-min retention; (E) 65%, 16.0-min retention. Preparative GC (Apiezon L) permitted purification (98%) of each isomer. For (Z)-1-(o-tolyl)propene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.7 (d of d, 3 H, J = 7, 2 Hz), 2.2 (s, 3 H), 5.5–6.7 (m, 2 H), 7.1 (s, 4 H). For (E)-1-(o-tolyl)propene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.8 (d of d, 3 H, J = 6.5, 2 Hz), 2.2 (s, 3 H), 5.7–6.3 (m, 1 H), 6.4–6.8 (m, 1 H), 6.9–7.5 (m, 4 H).

Isomerization of 1 at 175 °C. To 0.4 mL of 0.41 M potassium tert-butoxide in tert-butyl alcohol was added 60 mg of 1. The reaction tube was sealed in vacuo and heated at 175 °C for 11.5 h. After being cooled to -78 °C, the tube was broken, and the contents were poured into ether. The ethereal phase was washed with water, 4% aqueous HCl solution, and saturated aqueous NaCl solution and dried (MgSO<sub>4</sub>). Analytical GC (XF-1150) showed five peaks with relative areas (according to order of elution) of 1:12:6:4:76. Coinjection indicated that the first peak was 1 and third and last peaks were (Z)- and (E)-1-phenyl-1-butenes, re-

<sup>(10)</sup> Bragole, R. A. Ph.D. Dissertation, Yale University, New Haven, CT, 1965.

<sup>(11)</sup> Hurd, C. D.; Bollman, H. T. J. Am. Chem. Soc. 1933, 55, 699-702.

<sup>(12)</sup> Henne, A. L.; Matuszak, A. H. J. Am. Chem. Soc. 1944, 66, 1649-1652.

<sup>(13)</sup> Eisenlohr, F.; Schulz, L. Chem. Ber. 1924, 57, 1808-1820.

spectively. Preparative GC (Apiezon L) purification of the final (76%) component followed by <sup>1</sup>H NMR spectroscopy confirmed that this component was (E)-1-phenyl-1-butene. The second (12%) and fourth (4%) components were shown by GC coinjection not to be any of the other  $C_{10}H_{12}$  isomers on hand and were presumed to be (E)- and (Z)-1-phenyl-2-butenes, respectively. Isomerization of 2 at 70 °C. To 7.6 mL of 0.41 M potassium

tert-butoxide in tert-butyl alcohol was added 250 mg of 2 in 1 mL of tert-butyl alcohol. The mixture was heated in an oil bath at 70 °C, and 1-mL samples were removed at 3, 9, and 72 h. The samples were worked up as described above and analyzed by analytical GC (XF-1150); three components were present with area ratios as follows: time (ratio in order of elution), 3 h (6:27:67), 9 h (7:8:85), 72 h (8:<0.1:92). GC coinjection showed the peaks to be, respectively, (Z)-1-(o-tolyl)propene, 2, and (E)-1-(otolyl)propene. The first and third components were isolated by preparative GC (Apiezon L) and shown to be (Z)- and (E)-1-(otolyl)propenes, respectively, by <sup>1</sup>H NMR spectroscopy.

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Registry No. 1, 768-56-9; 2, 1587-04-8; allyl chloride, 107-05-1; benzyl bromide, 100-39-0; o-tolyl bromide, 95-46-5; benzaldehyde, 100-52-7; o-tolualdehyde, 104-87-0; (Z)-1-(o-tolyl)propene, 2077-33-0; (E)-1-phenyl-2-butene, 935-00-2; (Z)-1-phenyl-1-butene, 1560-09-4; (Z)-1-phenyl-2-butene, 15324-90-0; (E)-1-(o-tolyl)propene, 2077-34-1; (E)-1-phenyl-1-butene, 1005-64-7.

# Dehydrative Ring Closure of Some $\alpha$ -Pyrazolyl Ketones. Anomalous Closure of 1-Phenyl-1-[3-methyl-5-(2-naphthyl)pyrazolyl]acetophenone to 2-Methyl-4,5-diphenylbenzo[g]pyrazolo[5,1-a]isoquinoline

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During the past years we have been studying the intermolecular cycloaddition reactions of acyclic azines.<sup>2a</sup> The products obtained in these reactions are sharply in contrast with the intra- and intermolecular cycloaddition reactions observed for all carbon,<sup>3</sup> monoaza,<sup>4</sup> and other diaza<sup>5</sup> dienes.

The desired azines 3 were readily prepared by allowing  $\alpha$ -diketo monohydrazones 1 to react with the appropriate  $\alpha,\beta$ -unsaturated carbonyl species 2.<sup>6</sup> Cyclizations of the



azines produced, occurring at a variety of temperatures ranging from the reaction temperature of the formation of the azines 3 to 180 °C, gave N-substituted pyrazoles 4.6



In this note the preparation of a series of pyrazolo[5,1a]isoquinolines 5 (and 6) by the dehydrative ring closure of the corresponding pyrazoles 4 (Table I) is reported. The X-ray analysis of the major, anomalous, ring-closure product from 4d is discussed.

The normal ring closure of a large number of  $\beta$ -naphthyl derivatives by cyclodehydration have yielded compounds obtained by attack, mostly or exclusively, at the  $\alpha$  position of the naphthyl moiety.<sup>7</sup> Therefore, we expected that the dehydrative ring closure of the pyrazole species 4d with a  $\beta$ -naphthyl substituent in the 5 position ( $\overline{R}_3$ ) would yield the diaza steroidal backbone, 6a, with nitrogens in the 13 and 17 positions. A number of diazasteroids<sup>8</sup> have been prepared although none with this particular orientation of the nitrogen atoms.

Treatment of the 1-phenyl-[3-methyl-5-(2-naphthyl)pyrazolyl]acetophenone (4d) with polyphosphoric acid followed by quenching in water gave two products: one soluble in methylene chloride (81% yield) and one insoluble in methylene chloride (5% yield).

The structures of the two products were related, as shown by the <sup>1</sup>H NMR spectra (Table II); however, we could not determine if the ring closure to give the major product occurred in the normal manner to give 6a or if it gave 6b. Adequate quantities of the sample we list in Tables I and II as 6a were not available in order to obtain a correct analyses, therefore the assignment of the steroidal backbone for this structure is only presumed. In order to determine the structure of the major product, the methylene chloride soluble fraction, it was submitted to an X-ray analysis. The X-ray crystallographic analysis<sup>9</sup> of the major product showed that its structure was 6b, what we would designate as the abnormal<sup>7</sup> ring closure product.

 <sup>(</sup>a) University of Delaware;
 (b) Institute for Cancer Research.
 (c) (a) E. E. Schweizer and S. Evans, J. Org. Chem., 43, 4328 (1978), and references cited therein. (b) See Th. Wagner-Jauregg, Synthesis, 349

<sup>(1976),</sup> for review of azine cycloaddition chemistry.
(3) H. L. Holmes, Org. React., 4, 60 (1948).
(4) S. B. Needleman and M. C. Chang-Kuo, Chem. Rev., 62, 405 (1962); P. G. Sammes and R. A. Watt, J. Chem. Soc., Chem. Commun., 502 (1975); A. Demoulin, H. Gorissen, A. M. Hesbain-Frisque, and L. Ghosez, J. Am. Chem. Soc., 97, 4409 (1975).

<sup>(5)</sup> S. Somer, Tetrahedron Lett., 117 (1977); Angew. Chem., Int. Ed.
(5) S. Somer, Tetrahedron Lett., 117 (1977); Angew. Chem., Int. Ed.
Engl., 16, 58 (1977); R. Faragher and T. C. Gilchrist, J. Chem. Soc., Chem.
Commun., 581 (1976); I. Matsuda, S. Yamamoto, and Y. Ishii, J. Chem.
Soc., Perkin Trans. 1, 1528 (1976); M. Sakamoto, K. Miyazawa, and T.
Tomimatsu, Chem. Pharm. Bull., 24, 2532 (1976).

<sup>(6)</sup> T. A. Albright, S. Evans, C. S. Kim, C. S. Labaw, A. B. Russiello, and E. E. Schweizer, J. Org. Chem., 42, 3691 (1977).
(7) K. G. Rutherford and M. S. Newman, J. Am. Chem. Soc., 79, 213 (1957); F. A. Vingiello, A. Borkovec, and W. Zalac, Ibid., 80, 1714 (1958); S. M. Mukherji and N. K. Bhattacharyya, J. Org. Chem., 17, 1202 (1952); L. F. Fieser, Org. React., 1, 129 (1942); I. C. Badhwar and K. Venkataraman, J. Chem. Soc., 2420 (1932).
(8) (a) C. Verchere and C. Viel, J. Heterocycl. Chem., 17, 49 (1980); (b) T. Yamazaki, K. Matoba and T. Imai, Ibid., 16, 517 (1979), and references cited therein; (c) A. A. Akhrem, F. A. Lakhvich, V. N. Pshenichnyi, O. F. Fakhvich, and B. B. Kuzmitskii, Dokl. Akad. Nauk SSR, 240, 595 (1978); Chem. Abstr., 89, 215649 (1978); (d) I. Y. Tao and R. T. Blickenstaff, J. Pharm. Sci., 67, 283 (1978); (e) V. Gomez-Parta, An. R. Acad. Farm., 42, 609 (1976); Chem. Abstr., 86, 102512 (1976); (f) H. O. Huisman and N. N. Speckamp, Int. Rev. Sci.: Org. Chem., Ser. Two, 8, 207-36 (1976); (b) X. D. Berlin, N. N. Durham and C. Desjardins, U.S. Patent 3987 055 (1976); Chem. Abstr., 86, P106893 (1976). (9) W. Stallings, M. Nelson, and E. E. Schweizer, in preparation. (9) W. Stallings, M. Nelson, and E. E. Schweizer, in preparation.