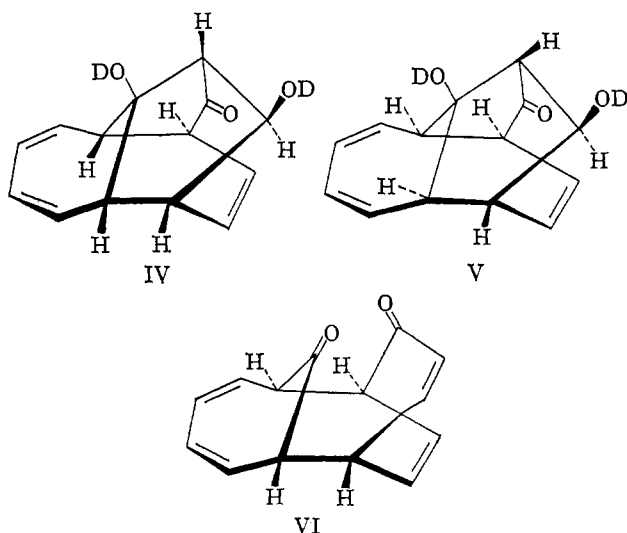


Figure 1. Nmr spectrum at 100 MHz of compound III in pyridine- $d_5$ ; scale is in parts per million downfield from internal tetramethylsilane.

hydration product confirms structure III. Spin decoupling demonstrates the homoallylic coupling  $|J_{DF}| = 3.4$  Hz<sup>7</sup> and the vicinal couplings  $|J_{AF}| = 5.6$  Hz and  $|J_{BD}| = 5.4$  Hz.<sup>8</sup> The vicinal couplings require the stereochemistry of the ABDF region to be as depicted in structure III. Such alternatives as IV or V are nearly strain free but should exhibit dissimilar values for  $J_{AF}$  vs.  $J_{BD}$ . Because epimerization of protons A, B, D, or F could not have occurred during formation of III, the stereochemistry of photodimer I must parallel that of III, as shown in formula VI.<sup>9</sup>



Since proton C is not coupled to the olefinic region or to proton F, the narrow C triplet must arise from long-range coupling of the W type<sup>10</sup> to both protons A and B, with  $|J_{AC}| = |J_{BC}| = 1.8$  Hz. The identity of proton C is confirmed by the following evidence. The prolonged action of deuterated base upon the 201° hy-

(7) Compare, for example, the 3.5-Hz homoallylic coupling in eleutherin reported by D. W. Cameron, G. I. Kingston, N. Sheppard, and Lord Todd, *J. Chem. Soc.*, 98 (1964).

(8) The respective assignments of vicinal pairs AF and BD in terms of formula III are arbitrary since present data do not allow reliable distinction between the two possibilities. The reversed assignment would not invalidate our stereochemical argument.

(9) Stereochemistry VI has been recently proposed by T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Letters*, 1397 (1967), on the basis of nmr data on the photodimer which exclude a skeletal stereochemistry corresponding to V. These workers, however, do not appear to have considered the alternative having the stereochemistry corresponding to *trans* derivative IV.

(10) See J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, 83, 2769 (1961).

dration product II or the 187° product III produces a *C-monodeuterated* compound  $C_{14}H_{13}DO_3$  which exhibits an nmr spectrum identical with that of III except for the absence of the signal for C near  $\delta$  3.4. Control experiments establish that this compound is simply III- $d_1$ ; thus, kinetically controlled hydration of photodimer I gives predominantly II whereas the thermodynamic product is the tetracyclic ketone III, and the observed isotopic exchange of proton C probably occurs through a retroaldol equilibrium. The stereochemistry of the secondary hydroxyl group in III is provisionally assigned as depicted since vicinal couplings CE or ED are not observed.

**Reaction Multiplicity.** Stereochemistry VI requires photoaddition of the first tropone molecule to the second in a *cis* manner. The question then arises whether this  $(6 + 4)$   $\pi$  cycloaddition is a concerted or stepwise process. It can be shown that with light above 300 m $\mu$  the rate of tropone disappearance (0.04 M) is unaffected by the presence of 0.1 M naphthalene ( $E_T = 61$  kcal). However, the use of ferrocene as quencher at 0.02 M concentration completely arrests the photodimerization process. Anthracene ( $E_T = 41$  kcal) at this concentration also quenches the disappearance of tropone and further serves to implicate a triplet intermediate in the reaction. Moreover, fluorenone ( $E_T = 53$  kcal) efficiently sensitizes the photodimerization of tropone. Under conditions such that fluorenone absorbs 70–80% of incident light, the disappearance of tropone has a relative quantum yield approximately 85% of that for the direct irradiation, and the sensitized reaction produces the three known photodimers<sup>1</sup> in the same ratio as observed in the direct reaction. Since no change in the relative proportions of the three dimers occurs during direct photodimerization, no one dimer is a precursor of another. All of these observations implicate a triplet of energy between 41 and 53 kcal as the principal intermediate leading not only to the major dimer VI but also to the other two dimers present in the mixture. Since the excited reactive species has triplet multiplicity, the *concerted* formation of both new  $\sigma$  bonds in the generation of VI is improbable, and the apparent formal violation of the Hoffmann–Woodward rules is accommodated by a *stepwise* process. Tropone thus joins cyclopentenone<sup>11</sup> and cyclohexenone<sup>12</sup> among the unsaturated ketones which undergo photodimerization by triplet intermediates.

(11) P. E. Eaton and W. S. Hurt, *ibid.*, 88, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, 88, 5672 (1966).

(12) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, 89, 3482 (1967).

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Received June 15, 1967

## The Reaction of Amine Anions with *p*-Toluenesulfonyl Azide. A Novel Azide Synthesis

Sir:

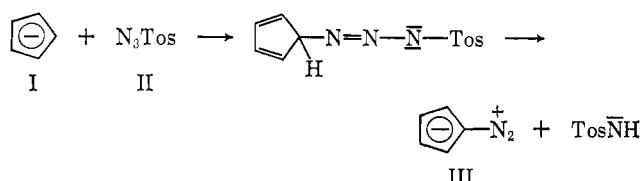
Since its initial disclosure in 1953, the elegant procedure of Doering and De Puy<sup>1</sup> for the preparation of

Table I. Data on Preparation of Azides

Amine (30 mmoles)	Azide, <sup>a</sup> % yield	Bp, °C (mm)	Triphenylphosphine adduct, mp, °C	Recovered <sup>i</sup> TosN <sub>3</sub> , %	TosNH <sub>2</sub> , %
Aniline	44	31–32 (1) <sup>b</sup>	131–132 <sup>f</sup>	18.3	61
<i>p</i> -Toluidine	49	50–52 (2) <sup>d</sup>	134–135 <sup>e</sup>	13.3	36
<i>p</i> -Chloroaniline	48	71–73 (3) <sup>e</sup>	119–120 <sup>h</sup>	15.0	66
Benzylamine	26	62–63 (4) <sup>c</sup>	...	15.0	36

<sup>a</sup> Yields are based on the amount of unrecovered *p*-toluenesulfonyl azide. <sup>b</sup> F. Moulin, *Helv. Chim. Acta*, **35**, 167 (1952), gives bp 53.5° (10 mm). <sup>c</sup> F. Moulin, *ibid.*, **35**, 167 (1952), gives bp 71–71.5° (13 mm). <sup>d</sup> S. Maffei and L. Coda, *Gazz. Chim. Ital.*, **85**, 1300 (1955), gives bp 80–81° (10 mm). <sup>e</sup> S. Maffei and L. Coda, *ibid.*, **85**, 1300 (1955), gives bp 90° (15 mm). <sup>f</sup> H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919), gives mp 130–132°. <sup>g</sup> L. Horner and H. Oedingen, *Ann.*, **627**, 142 (1959). <sup>h</sup> L. Horner and A. Gross, *ibid.*, **591**, 117 (1955). <sup>i</sup> Determined as the triphenylphosphine adduct.

diazocyclopentadiene (III) has remained something of a curiosity. The reaction essentially transfers two nitrogen atoms from *p*-toluenesulfonyl azide (II) to the anion I with the elimination of a hydrogen atom and *p*-toluenesulfonamide anion. However, Regitz<sup>2</sup> and

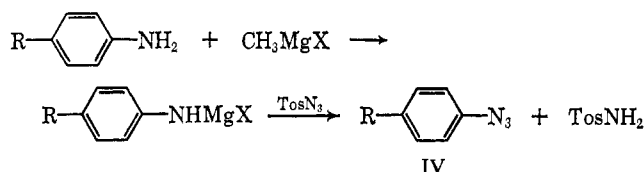


others<sup>3</sup> have in the past few years utilized this reaction to good advantage for the preparation of diazoalkane derivatives having substituents capable of stabilizing a negative charge. Farnum and Yates<sup>4</sup> have reported a similar transfer of the diazo function. The action of diazoacetophenone on sodium methyl phenylacetate gave methyl  $\alpha$ -diazophenylacetate.

Our current interest in the chemistry of azides coupled with our desire to develop new and specific methods to prepare azides has suggested this type of reaction as a potentially useful route to azides. Azides can formally be considered as diazoamines and, by analogy, the reaction of an amine anion with *p*-toluenesulfonyl azide should result in the formation of the azide derived from the amine (see Table I).

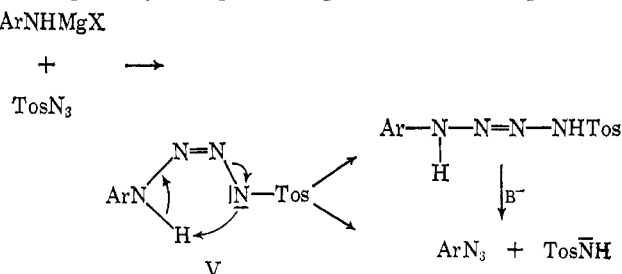
This expectation has been realized. Phenyl azide was obtained from the reaction of the halomagnesium salt of aniline with *p*-toluenesulfonyl azide. The yield was 44% based on the amount of unrecovered *p*-toluenesulfonyl azide. Phenyl azide (IV, R = H) was characterized by its boiling point, comparison of its infrared spectrum with that of an authentic sample, and its conversion to the triphenylphosphine adduct. Similarly, *p*-tolyl azide (IV, R = CH<sub>3</sub>) and *p*-chlorophenyl azide (IV, R = Cl) were prepared in 49 and 48% yields, respectively. They were identified by their boiling points, their infrared spectra, and their conversion to the triphenylphosphine adducts.

Although no extensive investigation has been carried out, aliphatic amines are apparently amenable to this



reaction, as evidenced by the formation of benzyl azide in 26% yield. No attempt was made to optimize the yield. The halomagnesium salt of *p*-nitroaniline gave a very low yield of *p*-nitrophenyl azide which was identified by the presence of a second azide band in the infrared spectrum of the reaction mixture. The salt of benzamide failed to give any detectable amount of benzazide.

The reaction may be viewed as proceeding *via* the formation of an intermediate triazene anion V which may decompose by two paths to give the observed products.



In every case where the azides were obtained, *p*-toluenesulfonamide was isolated by acidification of the aqueous phase.

The cyclic process may be related to the spontaneous decomposition of N-alkyl-N-nitroso carboxamides and sulfonamides to give diazoalkanes and the corresponding acids.<sup>5</sup>

**Acknowledgment.** The generous support of this work by the National Institutes of Health under Grant GM 13689-01 is hereby acknowledged with deep appreciation.

(5) E. H. White and C. A. Aufdermarsh, *J. Am. Chem. Soc.*, **83**, 1174, 1179 (1961).

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Received June 15, 1967

## The Carbonylation of Thexyldialkylboranes. A New General Synthesis of Ketones

Sir:

The thexyl group (2,3-dimethyl-2-butyl) exhibits an unusually low aptitude for migration in the carbonyla-

(1) W. E. Doering and C. H. De Puy, *J. Am. Chem. Soc.*, **75**, 5955 (1953); see also O. Dimroth, *Ann.*, **364**, 183 (1909); **373**, 349 (1910); **377**, 127 (1910); T. Curtius, *et al.*, *J. Prakt. Chem.*, **106**, 66 (1923); T. Curtius and W. Klavehn, *ibid.*, **112**, 65 (1926).

(2) M. Regitz, *Chem. Ber.*, **99**, 3128 (1965), and references therein.

(3) J. M. Tedder and B. Webster, *J. Chem. Soc.*, 4417 (1960); T. Weil and M. Cais, *J. Org. Chem.*, **28**, 2472 (1963); F. Klages and K. Bott, *Chem. Ber.*, **97**, 735 (1964); M. Rosenberger, P. Yates, J. B. Hendrickson, and W. Wolf, *Tetrahedron Letters*, 2285 (1964); A. M. von Leusen, P. M. Smid, and J. Strating, *ibid.*, 337 (1965); J. Kucera and Z. Arnold, *ibid.*, 1109 (1966).

(4) D. G. Farnum and P. Yates, *Proc. Chem. Soc.*, 224 (1960).