Table I. Data on Preparation of Azides

Amine (30 mmoles)	Azide,[a] % yield	Bp, °C (mm)	Triphenylphosphine adduct, mp, °C	Recovered[i] TosN₃, %	TosNH₂, %
Aniline	44	31–32 (1)[b]	131–132[f]	18.3	61
p-Toluidine	49	50–52 (2)[d]	134–135[g]	13.3	36
p-Chloroaniline	48	71–73 (3)[e]	119–120[h]	15.0	66
Benzylamine	26	62–63 (4)[c]	. . .	15.0	36

[a] Yields are based on the amount of unrecovered p-toluenesulfonyl azide. [b] F. Moulin, Helv. Chim. Acta, 35, 167 (1952), gives bp 53.5° (10 mm). [c] F. Moulin, ibid., 35, 167 (1952), gives bp 71–71.5° (13 mm). [d] S. Maffei and L. Coda, Gazz. Chim. Ital., 85, 1300 (1955), gives bp 80–81° (10 mm). [e] S. Maffei and L. Coda, ibid., 85, 1300 (1955), gives bp 90° (15 mm). [f] H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 635 (1919), gives mp 130–132°. [g] L. Horner and H. Oedinger, Ann., 627, 142 (1959). [h] L. Horner and A. Gross, ibid., 591, 117 (1955). [i] 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[2] and
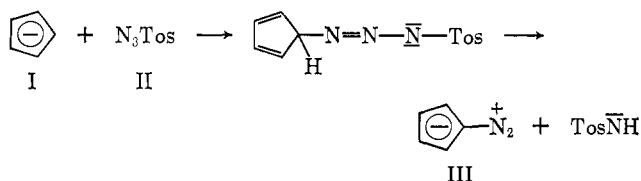
others[3] have in the past few years utilized this reaction to good advantage for the preparation of diazoalkane derivatives having substituents capable of stabilizing a negative charge. Farnum and Yates[4] have reported a similar transfer of the diazo function. The action of diazoacetophenone on sodium methyl phenylacetate gave methyl α-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-toluene-sulfonyl 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 = CH₃) 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.
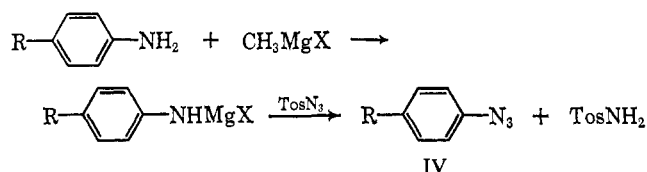
Although no extensive investigation has been carried out, aliphatic amines are apparently amenable to this

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.

ArNHMgX
+ ⟶
TosN₃

In every case where the azides were obtained, p-toluene-sulfonamide 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.[5]

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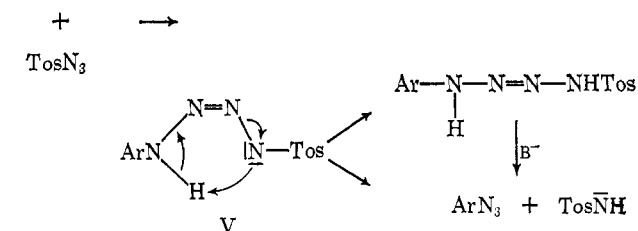
(4) D. G. Farnum and P. Yates, Proc. Chem. Soc., 224 (1960).

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

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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-

Table I. Results of the Carbonylation–Oxidation of Representative Thexyldialkylboranes

| Reaction | Product[a] | Physical properties | | Yield, % | |
		Bp (mm) or mp, °C	n^{20}D	Glpc	Isolated
V	Ethyl 7-methyl-5-oxo-octanoate	104 (4)[b]	1.4326	98	84
VI	Methyl 14-phenyl-12-oxo-tetradecanoate	56–57			73
VII	4-Cyclopentyl-4-oxo-butyl cyanide	106 (1.3)	1.4692	50	45
VIII	4-(exo-Norbornyl)-4-oxo-butyl chloride	88 (1.2)	1.4931	75	63

[a] All products yielded satisfactory elemental analyses and infrared and pmr spectra in agreement with the assigned structures. [b] Lit.[5] bp 120–122° (5 mm).

tion of mixed trialkylboranes. Consequently, the carbonylation of thexyldialkylboranes in the presence of water provides a new general synthesis of ketones capable of accommodating a wide range of functional groups.

It was previously shown that the controlled hydroboration of 2,3-dimethyl-2-butene provides a convenient synthesis of thexylborane (2,3-dimethyl-2-butylborane), an example of a highly hindered monoalkylborane, RBH₂[1,2] (I).

Thexylborane reacts with olefins in two distinct stages, first to form the thexylmonoalkylborane, and then to form the thexyldialkylborane[3] (II).

The discovery that the thexyl group does not migrate competitively in the carbonylation reaction in the manner exhibited by previous groups examined[4] makes it possible to convert the two olefins, Ol$_A$ and Ol$_B$, cleanly into the corresponding ketone R$_A$COR$_B$ (III).

Consequently, we are now in position to convert either the same olefin, or two different olefins, with a wide variety of functional groups, into the corresponding ketone with remarkable specificity (IV).

$$RCH=CH_2 + R'CH=CH_2 \longrightarrow RCH_2CH_2CCH_2CH_2R'$$
(with O double-bonded to the central carbon)

IV

The possibilities of this new synthesis are indicated by the following representative examples (V–VIII).

To realize the possible advantages of this new ketone synthesis, it is necessary merely to compare the present synthesis of ethyl 7-methyl-5-oxooctanoate (V) with the six-step literature procedure for the preparation of this compound.[5]

The experimental results are summarized in Table I.

In addition, we have experienced no difficulty in utilizing the method for the synthesis of simple dialkyl or cycloalkyl ketones, such as di-n-hexyl ketone, di-n-octyl ketone, cyclohexyl n-octyl ketone, etc., in yields of 70–90%. Perhaps even more exciting is the discovery that the procedure can be utilized to convert appropriate dienes into cyclic ketones.[6]

We encountered only one significant difficulty. In contrast to our earlier carbonylations which proceeded satisfactorily at atmospheric pressures,[4,7] the present carbonylations proved to be quite sluggish under these conditions. Consequently, the carbonylations were carried out in the usual pressure autoclave at 70 atm.

The following procedure for the synthesis of ethyl 7-methyl-5-oxooctanoate is representative.

(1) H. C. Brown and A. W. Moerikofer, J. Am. Chem. Soc., 84, 1478 (1962).
(2) H. C. Brown and G. J. Klender, Inorg. Chem., 1, 204 (1962).
(3) G. Zweifel and H. C. Brown, J. Am. Chem. Soc., 85, 2066 (1963).
(4) H. C. Brown and M. W. Rathke, ibid., 89, 4528 (1967).

(5) P. C. Bhattacharyya, J. Indian Chem. Soc., 42, 467 (1965).
(6) H. C. Brown and E. Negishi, J. Am. Chem. Soc., in print.
(7) H. C. Brown and M. W. Rathke, ibid., 89, 2737, 2738 (1967); M. W. Rathke and H. C. Brown, ibid., 89, 2740 (1967); H. C. Brown, G. W. Kabalka, and M. W. Rathke, ibid., 89, 4530 (1967).

A 300-ml round-bottomed flask, equipped with a rubber septum inlet, a thermometer well, a magnetic stirring bar, and a condenser[8] (the top of which provides an outlet attached to a mercury bubbler), was flushed with nitrogen. Into the flask was introduced 32.5 ml of 3.1 M borane in tetrahydrofuran (100 mmoles of BH_3). The flask was cooled to 0° and 8.7 g (103 mmoles) of 2,3-dimethyl-2-butene[9] was added to form the thexylborane. Stirring was continued for 1 hr at 0° to ensure completion of the reaction. Isobutylene (100 mmoles) dissolved in tetrahydrofuran was added and allowed to react at 0° for 30 min. Then 11.8 g (105 mmoles) of ethyl vinylacetate was added. The mixture was allowed to stand for 2 hr at 0°. Then 3.6 ml of water (200 mmoles) was added and the mixture was transferred into a 250-ml stainless steel autoclave under nitrogen. Carbonylation was achieved by filling the autoclave with carbon monoxide to 70 atm and maintaining at 50° for 3 hr. (Actually, the theoretical quantity of carbon monoxide was absorbed within 1 hr.) The material was transferred to a glass flask, 34 ml of 3 M sodium acetate (102 mmoles) was added, and oxidation carried out by the addition of 34 ml of 30% hydrogen peroxide. The rate of addition was controlled to maintain the temperature in the range of 30–40°. The reaction mixture was then maintained for 1 hr at 50° to ensure completion of the oxidation. After cooling, the aqueous layer was saturated with potassium carbonate and the organic phase was separated. The aqueous phase was again extracted with ether. After drying the combined extracts, distillation yielded 16.1 g (84%) of ethyl 7-methyl-5-oxooctanoate, bp 102–104° (4 mm), essentially pure by glpc and pmr examination.

(8) In our experiments the condenser was attached to a gas meter to permit a material balance on the utilization of hydride. However, this is not essential for the ordinary preparation.

(9) Originally we used material from the Phillips Petroleum Co. At the moment it is no longer available from that organization, so that we have been using material from Chemical Samples Co., Columbus, Ohio 43221.

(10) Postdoctorate Research Associate on a grant (GM-10937) supported by the National Institutes of Health.

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"Allylic Bromination" by N-Bromoacetamide. A Reexamination

Sir:

The Wohl–Ziegler reaction, allylic bromination by N-bromo amides and imides,[1] is so named because the definitive experiments by Ziegler[2] which established the unique effectiveness of N-bromosuccinimide (NBS) were prompted by Wohl's earlier work with N-bromoacetamide (NBA).[3] Although Ziegler confined his own observations on the NBA reaction to the comment that[2] "die von Wohl mitgeteilten Ergebnisse auf einen

(1) (a) C. Djerassi, Chem. Rev., 43, 271 (1948); (b) L. Horner and E. H. Winkelmann in "Newer Methods of Preparative Organic Chemistry," Vol. III, W. Forest, Ed., Academic Press Inc., New York, N. Y., 1964, p 151.

(2) K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelmann, Ann., 551, 80 (1942).

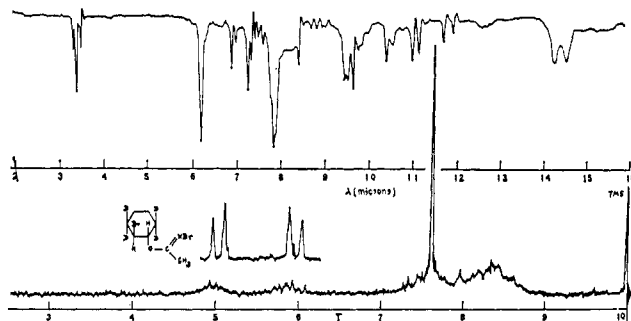(3) (a) A. Wohl, Ber., 52, 51 (1919); (b) A. Wohl and K. Jaschinowski, ibid., 54, 476 (1921).

Figure 1. Infrared and nmr spectra of 2-bromocyclohexyl N-bromoacetimidate.

nicht eben glatten Reaktionsverlauf schliessen lassen," Wohl's work has otherwise been universally accepted.[4–6]

We now report that the principal initial reaction of NBA with olefins is complete within minutes in refluxing carbon tetrachloride in the presence of light,[7] that this reaction produces isolable adducts of a new type, and that there is no allylic bromination. The stoichiometry of the addition reaction has been determined using varying molar ratios of olefin to NBA and has been found to be[8]

$$\text{olefin} + 2CH_3CONHBr \longrightarrow \text{adduct} + CH_3CONH_2 \quad (1)$$
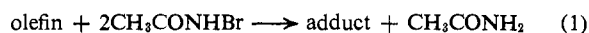
Thus, cyclohexene (4.1 g, 0.05 mole) in CCl_4 (10 ml) was added rapidly to a refluxing suspension of NBA (6.9 g, 0.05 mole) in CCl_4 (40 ml), refluxing being maintained by the heat of a photoflood lamp mounted underneath the reaction flask. Within 5 min the solid NBA had disappeared and droplets of acetamide could be seen. The colorless mixture was cooled in ice until crystallization of the acetamide was complete and this was then collected (1.54 g; 104% based on eq 1). The mother liquor was distilled under reduced pressure to a residue of 8.1 g. The distillate was found to contain 1.6 g of cyclohexene[9] (80%, based on eq 1). The residue, diluted with 30–60° petroleum ether (10 ml) and stored overnight at −20°, afforded 0.07 g (1%) of trans-2-acetamidocyclohexyl bromide (1), mp 110–111° (lit.[10] 109–110°). The filtrate was concentrated, ethyl ether (1 ml) was added, and this solution was kept overnight at −20°. The massive crystals then obtained weighed 2.64 g (36%)[11] and melted at 28.0–28.5°. The compound (Anal. Calcd for C_8H_{13}-$NOBr_2$: C, 32.12; H, 4.38; N, 4.72; Br, 53.46. Found: C, 32.34; H, 4.25; N, 4.69; Br, 53.57) is assigned structure 2 on the basis of this analysis and its infrared and nmr spectra, shown in Figure 1, together with the observation that thermal decomposition gives

(4) J. D. Park, H. J. Gerjovich, W. R. Lycan, and J. R. Lacher, J. Am. Chem. Soc., 74, 2189 (1952).

(5) R. E. Buckles, R. C. Johnson, and W. J. Probst, J. Org. Chem., 22, 55 (1957).

(6) E. Ucciani and M. Naudet, Bull. Soc. Chim. France, 1151 (1960).

(7) A 100-w photoflood No. 2 lamp with reflector was used.

(8) The substitution reaction envisaged by Wohl and others requires the formation of 1 mole of acetamide/mole of NBA. Buckles, et al.[5] were especially interested in this point but could recover only 55–65% of the theoretical amount of acetamide calculated on this basis.

(9) Determined by titration with a standardized solution of Br_2 in CCl_4.

(10) T. L. Cairns, P. J. Graham, P. L. Barrick, and R. S. Schreiber, J. Org. Chem., 17, 751 (1952).

(11) No attempt was made to optimize the recovery of crystalline material. The residue after removal of the adduct weighed 4.91 g (64%) and its infrared spectrum was identical with that of the crystals.