chloride in refluxing *tert*-butyl alcohol–potassium *tert*-butoxide gave only a 32% yield of cyclohexene, as determined by glc. This, however, is significantly better than the 7% yield reported for the Hofmann elimination from trimethylcyclohexylammonium chloride in the same medium.[9] When dimethyl sulfoxide was substituted for *tert*-butyl alcohol as the solvent, the yield was increased to 52%. Whether this is a solvation effect[10] or merely due to the higher boiling point of the solvent could not be ascertained, since cyclohexene cannot be distilled from the reaction mixture at 80° and direct injection into the heated port of a gas chromatograph would vitiate the attempt at temperature control.

The procedure reported here has several characteristics that may render it particularly advantageous for the degradation of amines and the synthesis of olefins: (a) the temperature required is lower than that usually employed in the Hofmann degradation and the yields were better, especially from the cyclic amine; (b) the conversion of a tertiary amine to a hydrazinium salt does not require strong oxidizing agents, as does the preparation of an amine oxide; (c) since the nitrogenous product of the elimination, a 1,1-disubstituted hydrazine, usually can be further alkylated at the 1-nitrogen atom to regenerate a hydrazinium salt,[11] sequential degradation by a repetetive methylation procedure should be possible, as in Hofmann's approach; (d) some of the side reactions encountered in the Cope reaction[12] are less likely with the aminimines. A probable disadvantage is that migrations from N-1 to N-2, especially of allylic and benzylic groups, may be expected.[13]

Experimental Section

Hydroxylamine-*O*-sulfonic acid was prepared by the method of Gösl and Meuwsen.[1b] Dimethyl-*sec*-butylamine was prepared by Eschweiler–Clarke methylation of *sec*-butylamine. The dimethylcyclohexylamine was a commercial sample.

Dimethyl-*sec*-butylhydrazinium Chloride. Dimethyl-*sec*-butylamine (5 g, 50 mmol) was suspended in a vigorously stirred cold solution of 8 g of potassium carbonate sesquihydrate (50 mmol) in 20 ml of water containing 0.1 g of EDTA. A cold solution of 5.6 g (50 mmol) of hydroxylamine-*O*-sulfonic acid in 10 ml of water was added over 40 min. Methanol (180 ml) was added and the precipitated K_2SO_4 was filtered. The filtrate was adjusted to pH 7 by addition of hydrochloric acid, and the solvent was removed in a rotary evaporator. Acetone was added to the syrupy residue to promote crystallization of the hydrazinium chloride. The salt was purified by dissolving in methanol, filtering to remove a small amount of K_2SO_4, evaporating, and reprecipitating with acetone. After drying at 100° the product weighed 5.5 g (73%), mp 170°.

Anal. Calcd for $C_6H_{17}N_2Cl$: N, 18.37. Found: N, 18.36.

Nmr ($CDCl_3$) δ 6.75 (br, 2 H, NH_2), 3.7 (br, 1 H), 3.50 [d, 6 H, $N(CH_3)_2$], 1.46 (d, 3 H + 1 H), 1.05 (t, 3 H). The C-3 methylene of the *sec*-butyl group appears to be widely split by the adjacent chiral atom into two broad regions, one centered at δ 2.35 (1 H) and the other buried under the C-1 methyl doublet at δ 1.46.

Dimethylcyclohexylhydrazinium Chloride. Following a similar procedure, 6.35 g (50 mmol) of dimethylcyclohexylamine gave 3.2 g (35%) of the hydrazinium salt: mp 225–227°; nmr ($CDCl_3$) δ 6.75 (br, 2 H, NH_2), 3.75 (br, 1 H), 3.50 [s, 6 H, $N(CH_3)_2$], 2.47 (br, 2 H, 2,6-equatorial), 1.97 (br, 2 H, 2,6-axial), 1.8–1.3 (m, br, 6 H).

Anal. Calcd for $C_8H_{19}N_2Cl$: N, 15.70. Found: N, 15.68.

When 2 equiv of either of the hydrazinium salts was added to 0.1 *N* NaOH, the pH as determined by a glass electrode remained at 13; therefore the pK_a's of these compounds must be at least that great.

Eliminations. A. To a solution of 2.25 g (20 mmol) of potassium *tert*-butoxide in 10 ml of *tert*-butyl alcohol was added 2.42 g (16 mmol) of dimethyl-*sec*-butylhydrazinium chloride. The mixture was refluxed for 90 min, using a slow stream of nitrogen to sweep the gaseous products through the condenser into a Dry Ice cooled trap. The contents of the trap were transferred to a chilled vial and weighed, yield 0.58 g (73%). The nmr spectrum indicated that the material collected consisted solely of the isomeric *n*-butenes. The ratio of isomers was determined by glc on a 6 ft × 0.125 in. column packed with saturated $AgNO_3$ in phenylacetonitrile supported on 80–100 mesh Chromosorb P, using a flame ionization detector and electronic integration.

B. Dimethylcyclohexylhydrazinium chloride, 1.6 g (9 mmol), was added to a solution of 1.2 g (10 mmol) of potassium *tert*-butoxide in 15 ml of *tert*-butyl alcohol and the mixture was refluxed for 3 hr. The presence of cyclohexene was indicated by the nmr of the reaction mixture, and the amount was determined by glc on a 6-ft silicone (SE-30) column, using toluene as an internal standard, yield 0.24 g (32%).

C. Two grams (11 mmol) of dimethylcyclohexylhydrazinium chloride was added to a solution of 1.3 g (12 mmol) of potassium *tert*-butoxide in 15 ml of dimethyl sulfoxide, and the mixture was refluxed for 90 min. After cooling, glc indicated a 52% yield of cyclohexene.

Registry No.—Dimethyl-*sec*-butylhydrazinium chloride, 51051-67-3; dimethyl-*sec*-butylamine, 921-04-0; hydroxylamine-*O*-sulfonic acid, 2950-43-8; dimethylcyclohexylhydrazinium chloride, 51051-68-4; dimethylcyclohexylamine, 98-94-2.

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A Convenient Synthesis of Primary Benzhydrylamines

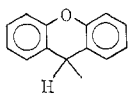
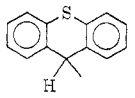
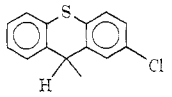
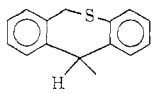
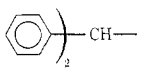
James E. Ollmann and Donald T. Witiak*

Division of Medicinal Chemistry, College of Pharmacy, The Ohio State University, Columbus, Ohio 43210

Received November 21, 1973

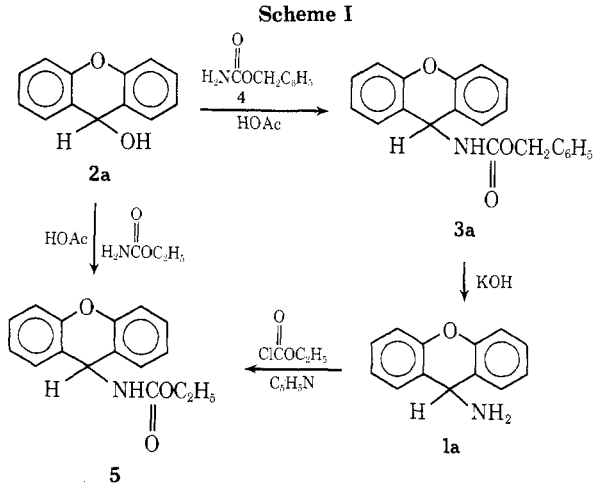
Our need for relatively large quantities of primary benzhydrylamines (**1**) prompted the search for a general synthetic pathway. The well-known condensation of xanthydrol (**2a**) with primary amides[1] appeared to be a good method for bonding nitrogen to the benzhydryl position. Though previous attempts to hydrolyze *N*-9-xanthylacetamide to amine **1a** failed,[2] **1a** has recently been prepared by alkaline hydrolysis of the corresponding ethyl carbamate (**5**).[3] Similarly, we have found that benzyl *N*-9-xanthylcarbamate (**3a**), prepared from **2a** and benzyl carbamate (**4**),[4] is readily hydrolyzed to 9-aminoxanthene (**1a**) by refluxing in 95% EtOH containing 15% KOH. That amine **1a** was indeed obtained was shown by its conversion to carbamate **5** (Scheme I), identical in every respect with the compound obtained by condensation of **2a** with urethane.

Table I
Synthesis and Hydrolysis of Substituted Benzyl *N*-Benzhydrylcarbamates (3a–e)

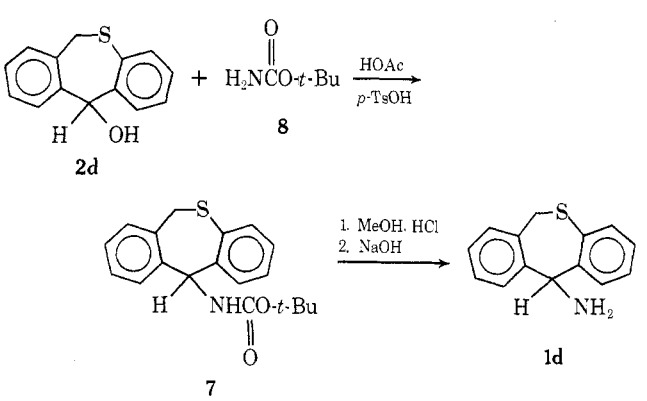
Benzhydrols ROH (2)	Product benzyl carbamates RNHCO$_2$CH$_2$C$_6$H$_5$ (3)[a] Condensation reaction time (hr)[b]	Mp, °C	Yield, %	Benzhydrylammonium acetates RNH$_3^+$ $^-$OAc (6) Hydrolysis time (hr)[c]	Mp, °C (lit. mp)	Yield, %
2a, R = 	2	165–166	87	24	153–154 dec (150–151 dec)[d]	76
2b, R = 	12	134–135	74	6	155–157 dec (152)[d]	78
2c, R = 	12[e]	132–134	71	3.5	153–155 dec[f]	55
2d, R = 	0.75[g]	179–180	82	1		None
2e, R = 	18[h]	116–118	85	4	140–141 (141)[i]	94

[a] Satisfactory analytical data were reported for all new compounds listed. [b] Reactions run at 25° in HOAc with *ca.* 20 mol % excess of benzyl carbamate (4). [c] In refluxing 95% EtOH containing 15% KOH. [d] Reference 2. [e] Prior to work-up the reaction mixture was heated at 90° for 30 min. [f] Free amine **1c** mp 67–69°. *Anal.* Calcd for $C_{13}H_{10}ClNS$: C, 63.03; H, 4.07; Cl, 14.31; N, 5.65; S, 12.94. Found: C, 62.69; H, 4.08; Cl, 14.21; N, 5.71; S, 13.34. [g] *p*-TsOH (50 mg) was required as catalyst. [h] Concentrated H_2SO_4 (0.2 ml) added as catalyst. [i] Reference 11.

Scheme I



Scheme II



The condensation of various benzhydrols with benzyl carbamate (4) in glacial HOAc appears to be a rather general reaction. The results of several such condensations, some of which require a catalytic amount of strong acid, are summarized in Table I. The results obtained from the basic hydrolysis of the benzyl carbamates, **3**, are also shown in Table I.

Owing to the instability of several of the product amines in aqueous acid[2] and the difficulties experienced when attempting to separate the reaction products (amines plus benzyl alcohol) by conventional ether–water extraction techniques, the desired analogs **1** were generally isolated by precipitating the acetate salts (**6a–c,e**) from hexane solution. Several attempts to hydrolyze the dihydrodibenzo[*b,e*]thiepin analog **3d** in basic medium (*i.e.*, reactions were run at room temperature or at reflux with varying concentrations of KOH for periods of 1 hr to 1 week) only afforded complex mixtures apparently containing some thiepin ring-opened products. Treatment of **3d** with HBr in HOAc by the method of Ben-Ishai and Berger[5] afforded only unreacted starting material. For these reasons, carbamate **7** containing the more acid labile *tert*-butyloxy function was synthesized (Scheme II). Condensation of *tert*-butyl carbamate (**8**)[6] with alcohol **2d** afforded **7** in 52% yield. Amine **1d** was obtained in 58% yield by acid-catalyzed hydrolysis of carbamate **7**.

Experimental Section

Materials. Xanthydrol (**2a**),[7] 10-thioxanthydrol (**2b**),[8] 2-chloro-10-thioxanthydrol (**2c**),[9] 6,11-dihydrodibenzo[*b,e*]thiepin-11-ol (**2d**),[10] benzyl carbamate (**4**),[4] and *tert*-butyl carbamate (**8**)[6] were all prepared by methods reported in the literature.

Because of the generality of the methods for both the condensation and hydrolysis reactions, only two examples of each will be given.

Benzyl *N*-Benzhydrylcarbamate (3e). To a solution of 2.0 g (0.011 mol) of benzhydrol and 2.0 g (0.013 mol) of benzylcarbamate in 25 ml of glacial HOAc was added 0.2 ml of concentrated H_2SO_4. The mixture was stirred at room temperature for 18 hr and poured into H_2O (150 ml) and the precipitate was collected. The product was recrystallized from aqueous EtOH affording 2.94 g (85%) of the desired carbamate **3e** as white needles, mp 116–118°.

Benzhydrylammonium Acetate (6e). To a solution of KOH (5 g, 0.09 mol) in 50 ml of 95% EtOH was added 1.56 g (0.005 mol) of benzyl *N*-benzhydrylcarbamate (**3e**). The mixture was heated at reflux for 4 hr, cooled, and concentrated under reduced pressure to a volume of *ca.* 15 ml. The concentrate was shaken with 75 ml of H_2O and extracted with Et_2O. The organic layer was washed

with H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The residual oil was dissolved in 200 ml of hexane. HOAc (1 ml) was added slowly with constant stirring. The white precipitate was collected, washed with hexane, and air-dried affording 1.11 g (94%) of acetate **6e**, mp 140–141° (lit.[11] mp 141°).

2-(2-Methylpropyl) *N*-[11-(6,11-Dihydrodibenzo[*b*,*e*]thiepin)]-carbamate (7). A solution of 2.28 g (0.010 mol) of freshly recrystallized 6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol (**2d**), 1.5 g (0.013 mol) of *tert*-butyl carbamate (**8**), and 50 mg of *p*-toluenesulfonic acid in 25 ml of HOAc was stirred at 25° for 1 hr. The mixture was poured into H_2O (50 ml) and allowed to stand for 30 min; the solid was collected by filtration and recrystallized from EtOH affording 1.7 g (52%) of carbamate **7** as white needles, mp 168–170°.

Anal. Calcd for $C_{19}H_{21}NO_2S$: C, 69.69; H, 6.46; N, 4.28; S, 9.79. Found: C, 69.48; H, 6.44; N, 4.24; S, 10.07.

11-Amino-6,11-dihydrodibenzo[*b*,*e*]thiepin (1d). To a solution of 0.65 g (0.002 mol) of carbamate **7** in 30 ml of MeOH was added 2.5 ml of 12 *N* HCl. The mixture was heated at reflux for 15 min, cooled, and concentrated under reduced pressure. The residue was partitioned between 5% NaOH and Et_2O. The organic layer was washed with H_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was recrystallized from absolute EtOH affording 0.26 g (58%) of off-white crystalline amine **1d**, mp 146–147° (lit.[10] mp 149–150°).

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Registry No.—**1c**, 51065-24-8; **1d**, 1745-53-5; **2a**, 90-46-0; **2b**, 6783-74-0; **2c**, 6470-02-6; **2d**, 1745-46-6; **2e**, 91-01-0; **3a**, 6331-77-7; **3b**, 51065-25-9; **3c**, 51065-26-0; **3d**, 51065-27-1; **3e**, 5180-34-7; **4**, 621-84-1; **6a**, 51065-28-2; **6b**, 51065-29-3; **6c**, 51065-30-6; **6e**, 51065-31-7; **7**, 51065-32-8; **8**, 4248-19-5.

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The Azido Transfer Reaction to Aliphatic Carbons

S. J. Weininger* and S. Kohen

Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

S. Mataka, G. Koga, and J.-P. Anselme*

Department of Chemistry, University of Massachusetts at Boston, Boston, Massachusetts 02125

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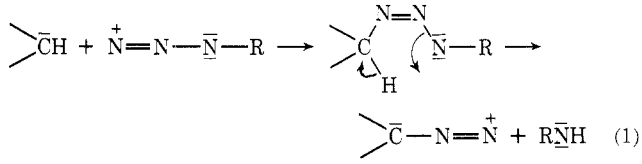
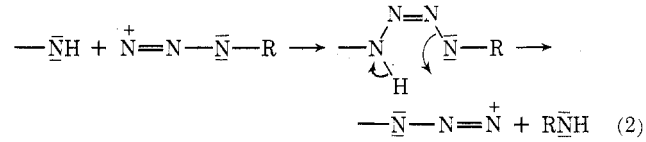
The *diazo transfer* reaction (eq 1), originally studied by Dimroth[1] and Curtius,[2] remained dormant until its epochal revival by Doering and De Puy in 1953.[3] Since that time, it has become a well-established route to α-diazocarbonyl compounds, largely through the extensive work of Regitz and his group.[4] This reaction has recently been developed into an azide synthesis[5] by the use of anions of primary amines,[6] hydrazines,[7] and hydrazones (eq 2).[8]



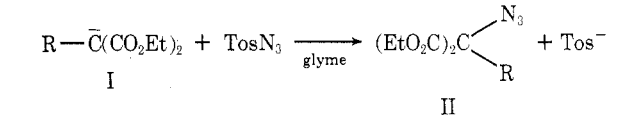
(1)



(2)

Although other diazo transfer agents such as nitrous oxide,[9] various azides,[10] azidinium salts,[11] and diazoalkanes[12] have been investigated, the most widely used reagent has been *p*-toluenesulfonyl azide (tosyl azide).[13] The availability of *three* nitrogens, coupled with the good nucleofugal property of the *p*-toluenesulfinate ion, suggests that sulfonyl azides should also be capable of acting as *azido transfer agent*. Indeed, the azido group has been transferred to anions having no α hydrogen[14a-e] or an α-carbonyl group[14f-h] to permit completion of the diazo transfer step. The recent report of Reed and Lwowski[15] of an azido transfer to an aliphatic bridgehead carbanion prompts us to report our own results to broaden the scope of this reaction.

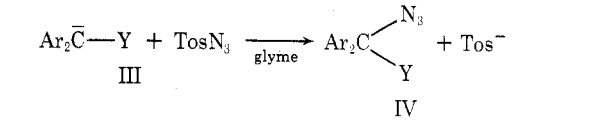
The reaction of the sodium salts of diethyl phenyl- and 7-cycloheptatrienylmalonate (Ia and Ib) with tosyl azide gave the corresponding azidomalonates (IIa and IIb) in 77 and 65% yields, respectively. The replacement of one



I II

a, R = Ph
b, R = 7-cycloheptatrienyl

carbethoxy group with the fluorenyl moiety did not affect the course of the reaction and 9-carbomethoxy-9-azidofluorene (IVa) was isolated in 57% yield. Similarly, α-azidodiphenylacetonitrile (IVb) was obtained from the reaction of the sodium salt of diphenylacetonitrile, albeit in only 18% yield of isolated product.[16]



III IV

a, Ar_2C = 9-fluorenyl; Y = CO_2Me
b, Ar = Ph; Y = CN

These results show the azido transfer reaction to be applicable to both aliphatic and aromatic anions, as well as secondary amine anions.[14b,c]

Experimental Section[17]

Diethyl Azidophenylmalonate (IIa). A solution of 5.0 g (0.021 mol) of diethyl phenylmalonate in 25 ml of dry glyme was dripped into a suspension of 0.82 g (0.021 mol) of sodium hydride (which was previously freed of mineral oil with ether and hexane) in 30 ml of dry glyme at room temperature. The reaction was carried out in a 150-ml three-neck flask equipped with a nitrogen inlet, a pressure-equalizing dropping funnel, a magnetic stirring bar, and a gas outlet. The apparatus was flushed with nitrogen prior to the addition of diethyl phenylmalonate. After gas evolution had stopped, a solution of 4.07 g (0.021 mol) of tosyl azide in 25 ml of dry glyme was dripped into the reaction mixture over a 30-min period. After the addition was complete, the mixture was stirred at 35–40° for 1 hr; a white solid started to precipitate at that time and stirring was continued for an additional 2 hr. The mixture was cooled and the solvent was evaporated on a rotary evaporator at 40° under reduced pressure. Ether (100 ml) and water (50 ml) were added to the pasty residue. The ethereal layer was separated, washed three times with 25-ml portions of water, and dried over sodium sulfate. A yellowish oil was obtained (4.5