diazepinone product must be **3**.[15] The nmr spectrum of **9**, as compared to that of **4**, can be accounted for by anisotropic shielding of the alkenyl protons by the bay proton on the naphthalene nucleus.

Careful examination of the reaction mixture and subsequent mother liquors from crystallizations failed to reveal the presence of any **2**. Interruption of the boiling xylene reaction in the hope of isolating **2** or other intermediates was unsuccessful. Condensation reactions carried out at lower temperatures also failed to give **2**; a similar product distribution of **3** and **4** was obtained in boiling toluene as solvent and in boiling benzene essentially no reaction occurred. We believe that the formation of **3** and **4** in this reaction can best be explained by considering that both diazepinone products **2** and **3** were initially formed. **3**, which was found to be resistant to thermal rearrangement, was not further affected by the reaction conditions. However, **2**, because of an apparently very low energy barrier for ring contraction, must have been converted immediately and quantitatively into **4**. Attempts to prepare **2** by an independent route in order to study its rearrangement unfortunately failed to give the desired product.

Catalytic reduction of **3** in acetic acid[4] afforded the tetrahydrodiazepinone **10**, mp 209°. This material was similar to but not identical with the tetrahydrodiazepinone, mp 229–230°, prepared by fusion of 1,2-diaminonaphthalene with crotonic acid, according to the procedure of Ried and Höhne.[4] The crotonic acid product is, therefore, correctly identified as **11**, and not **10** as previously suggested.[4]

## Experimental Section[16]

**1,5-Dihydro-2-methyl-4*H*-naphth[1,2-*b*][1,4]diazepin-4-one (3).**—Prepared according to the procedure of Ried and Höhne,[4] this material was previously described as **2**. It formed white crystals from xylene: mp 246°; nmr ($C_5D_5N$) $\delta$ 2.43 (3 H, s), 3.28 (2 H, s), and 7.42–7.70 ppm (6 H, multiple aromatic peaks); uv $\lambda_{max}^{ethanol}$ 243 nm ($\epsilon$ 55,700), 294 (7100), 308 (6900), 323 (4500), and 337 (4800). The presence of **2** in the reaction mixture could not be observed by spectral or tlc studies.

**1,2-Dihydro-3-isopropenyl-3*H*-naphth[1,2-*d*]imidazol-2-one (4).**—The ether-soluble product from the reaction of 1,2-diaminonaphthalene and ethyl acetoacetate by the Ried and Höhne procedure,[4] this material was erroneously reported to be **1**. It formed white crystals from cyclohexane: mp 198°; nmr ($CDCl_3$) (time averaged)[17] $\delta$ 2.48 (3 H, fine splitting), 5.53 (1 H, q, $J$ = 6 Hz), and 5.65 ppm (1 H, q, $J$ = 6 Hz); ir $\lambda_{max}^{KCl}$ 5.85 $\mu$.

**2-Isopropylamino-1-nitronaphthalene (7).**—2-Chloro-1-nitronaphthalene (**6**) was prepared from 2-amino-1-nitronaphthalene essentially according to the procedure of Hodgson and Leigh;[18] in place of steam distillation, the product was purified by crystallization from ligroin (bp 95–110°). A solution of 3.2 g of **6** and 32 g of isopropylamine in 70 ml of absolute ethanol was heated at 100° for 6 hr in a stainless steel bomb. The red reaction solution was taken to dryness and the residue was washed with water to remove isopropylamine hydrochloride. The water-insoluble product was crystallized once from benzene–petroleum ether (bp 60–90°) and once from cyclohexane to give 3.5 g (100%) of **7**, mp 104–105°.

*Anal.* Calcd for $C_{13}H_{14}N_2O_2$: C, 67.83; H, 6.08; N, 12.17. Found: C, 67.82; H, 5.81; N, 11.89.

**1-Amino-2-isopropylaminonaphthalene (8).**—A solution of **7** (350 mg) in 50 ml of absolute ethanol was shaken under hydrogen in the presence of 200 mg of 5% palladium on charcoal on a Parr apparatus for 30 min. The catalyst was separated and the filtrate was evaporated to dryness. The residue was crystallized from ligroin to give white crystals of **8**, yield 130 mg (42%), mp 102–103°.

*Anal.* Calcd for $C_{13}H_{16}N_2$: C, 78.00; H, 7.99; N, 13.99. Found: C, 78.28; H, 7.97; N, 14.02.

**1,2-Dihydro-3-isopropyl-3*H*-naphth[1,2-*d*]imidazol-2-one (5). Method A. Cyclization of 8.**—Phosgene was passed into 30 ml of xylene for 30 min at room temperature and to this solution was added, in small portions with stirring, 300 mg of **8**. Phosgene was again bubbled into the solution (15 min), following which the reaction mixture was warmed at 60° for 5 hr. After overnight standing, the clear, pale yellow solution was evaporated to dryness under reduced pressure and the residue was crystallized several times from cyclohexane to give 330 mg (97%) of white crystals: mp 200–201°; ir $\lambda_{max}^{KCl}$ 5.90 $\mu$; uv $\lambda_{max}^{ethanol}$ 246 nm ($\epsilon$ 67,300), 293 (3800), 305 (3500), and 340 (4000); nmr ($CDCl_3$) $\delta$ 1.66 (6 H, d, $J$ = 7 Hz), 4.98 (1 H, m, $J$ = 28 Hz), and 7.27–8.23 ppm (6 H, multiple aromatic peaks).

*Anal.* Calcd for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.25; N, 12.38. Found: C, 74.45; H, 6.33; N, 12.28.

**Method B. Reduction of 4.**—A solution of 125 mg of **4** in 40 ml of absolute ethanol was shaken overnight under hydrogen in the presence of 60 mg of platinum oxide. The catalyst was separated and the ethanolic filtrate was evaporated to give a brown oil, which was dissolved in hot cyclohexane. After treatment with charcoal, the solution was reduced to 10 ml and the white precipitate was collected and crystallized twice from cyclohexane to give material identical in all respects with that obtained by method A.

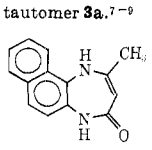
**2,3-Dihydro-1-isopropenyl-1*H*-naphth[1,2-*d*]imidazol-2-one (9).**—A 100-mg sample of **3** in a small test tube was heated at 250° for 3 hr in the absence of solvent. Upon cooling, the solidified mass was treated with warm (60°) benzene and the insoluble material (mostly unchanged **3**) was separated. Addition of petroleum ether to the benzene solution gave an off-white precipitate. This material was crystallized several times from benzene–petroleum ether to give 32 mg (32%) of **9** as small white crystals: mp 222°; ir $\lambda_{max}^{KCl}$ 5.88 $\mu$; nmr ($CDCl_3$) $\delta$ 2.30 (3 H, fine splitting), 5.43 (1 H, q, $J$ = 6 Hz), and 5.60 ppm (1 H, q, $J$ = 6 Hz).

*Anal.* Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.40; N, 12.49. Found: C, 75.17; H, 5.47; N, 12.62.

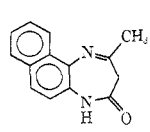
**Registry No.**—**3**, 35624-19-2; **4**, 35624-20-5; **5**, 35624-21-6; **7**, 35624-22-7; **8**, 35624-23-8; **9**, 35624-24-9; **11**, 35624-25-0; 1,2-diaminonaphthalene, 938-25-0; ethyl acetoacetate, 141-97-9; crotonic acid, 3724-65-0.

**Acknowledgment.**—We thank Mrs. Lynne C. Jones and Mrs. Marilyn A. Whitesell for technical assistance at different times during this work.

(15) Solutions of **3** in chloroform, pyridine, and dimethyl sulfoxide are bright yellow and the nmr spectrum is consistent with structure **3b**. However, the diazepinone, a white solid, probably exists in the solid state in the form of the leuco tautomer **3a**.[7-9]



**3a**



**3b**

(16) Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(17) The time-averaged spectrum was obtained by means of a Japan Electron Optics Laboratory Co. Model JRA-1 Spectrum Accumulator interfaced with a Varian Associates Model A-60 spectrometer.

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## Trifluoromethanesulfonyl Azide. Its Reaction with Alkyl Amines to Form Alkyl Azides

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*p*-Toluenesulfonyl azide is a widely used reagent for the transfer of the diazo group to active methylene

compounds.[1] The use of certain other sulfonyl azides for this purpose has been investigated by Hendrickson and Wolf,[2] who found that in some reactions product purification could be facilitated by the use of carboxybenzenesulfonyl azide. Chlorosulfonylbenzenesulfonyl azide was expected to be more reactive than toluenesulfonyl azide but was generally found to give lower yields.

In our study of sulfonyl leaving groups,[3] it occurred to us that the very great electron-withdrawing ability of the trifluoromethanesulfonyl (triflyl) group[4] might confer sufficient reactivity on triflyl azide that it could be used without basic promotion to diazotize active methylene compounds and with basic promotion to diazotize less active compounds. Triflyl azide was quickly produced by the reaction of triflic anhydride with aqueous sodium azide at 0° and separated into a water-insoluble, lower layer. After experiencing one explosion, we carried out subsequent preparations of the azide, without further trouble, in the presence of a solvent. The strong characteristic infrared spectrum of triflyl azide persisted even after 24 hr standing in methylene chloride, *N*,*N*-dimethylformamide, tetrahydrofuran, dimethyl sulfoxide, dioxane, acetonitrile, methanol, or acetone, indicating only slow, if any, reaction with these solvents. The characteristic infrared spectrum also persisted for at least several hours in the presence of potassium *tert*-butoxide, hydroxide, or fluoride, sodium methoxide or 2,6-lutidine indicating that it was only slowly destroyed by these bases. Despite these observations of reasonable stability, product yields using the new reagent (see below) were found to be significantly lower if the azide was prepared before use rather than in the presence of coreactant.

Although infrared spectral changes seemed to indicate that triflyl azide gave products of diazo transfer with 5,5-dimethylcyclohexa-1,3-dione, 1-benzoylacetone, and even cyclohexanone (all with or without a catalytic amount of 2,6-lutidine), none of the reaction conditions tried permitted the isolation of the desired products in reasonable yields.

Toluenesulfonyl and the less reactive azides do not react directly with primary amines but do form alkyl azides when treated with the Grignard[5] or lithium[6] salts of the amines. The utility of the new reagent is demonstrated in its ability to transfer the diazo group directly to the primary amine function to form the corresponding alkyl azide.

Alkyl azides are usually prepared by the displacement of halide, sulfate, or tertiary amine leaving groups by the azide ion.[7] Rearrangements and steric hindrance limit the scope of these reactions for tertiary azides, which can sometimes be produced by the solvolysis of the appropriate derivative in the presence of azide salts. Recently, the synthesis of secondary and tertiary alkyl azides has been achieved through mercuration of olefins in a solution containing azide salts;[8] however, this method is only effective for terminal and strained cyclic olefins. β-Haloalkyl and vinyl azides can be prepared from olefins and halo azides.[9] As outlined in the Experimental Section, the triflyl azide method has been successful for the preparation of *n*-hexyl azide and 2,4,4-trimethyl-2-pentyl azide in isolated yields of about 70%. *tert*-Butyl azide has also been prepared but an isolated yield was not determined. Reactions of *n*-hexyl amine in the absence of 2,6-lutidine generally give yields of 50% or lower and less pure products.

The fact that 2,2,4-trimethyl-2-pentyl trifluoromethanesulfonamide does not react with aqueous sodium azide under reaction conditions indicates further that the alkyl azide must be formed by diazo transfer from triflyl azide. Although the point remains to be established experimentally, it appears likely that triflyl azide would convert the amine to the azide with retention of configuration and should, therefore, be useful in the correlation of configurations of amines and azides. We are continuing to explore the apparent reaction of benzamide with triflyl azide in the presence of lutidine. Amides and magnesium salts of amides are apparently unreactive with other sulfonyl azides.

## Experimental Section

**Triflyl Azide.**—To a magnetically stirred solution of 8 g of $NaN_3$ in 20 ml of $H_2O$ over 25 ml of $CH_2Cl_2$ at 0° was added 7 g (0.025 mol) of trifluoromethanesulfonyl anhydride.[10] The low temperature and stirring were maintained for 2 hr, and trifluoromethanesulfonyl azide (triflyl azide) was found in the organic layer and in the first two extractions of the water layer with 10-ml portions of the solvent: ir 4.65, 7.1, 8–9 μ (three peaks); $^{19}F$ nmr 183 Hz at 94.6 MHz (capillary standard trifluoroacetic acid).

*Caution.*—The resulting sulfonyl azide conveniently separates from the water solution if no organic layer is present, but we experienced an explosion in one preparation of it without organic solvent.

***n*-Hexyl Azide.**—A sample of 0.5 ml (0.84 g) of freshly distilled trifluoromethanesulfonic anhydride was slowly added to 2 ml of 6.25 *N* aqueous $NaN_3$ over 0.375 g of *n*-hexyl amine and 0.162 g of 2,6-lutidine in 5 ml of $CH_2Cl_2$. The mixture was stirred and kept at 0° for 2 hr. The organic layer was extracted twice with concentrated aqueous KOH solution to remove the sulfonamide, with 0.5 *N* HCl until the extract was acidic to litmus, then with $H_2O$ until it was neutral. Evaporating the solvent left 0.251 g (66.3%) of *n*-hexyl azide: bp 81–83° (60 mm) [lit.[11] bp 85° (63 mm)]; ir 4.80 μ ($N_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 287 nm (ε 20) [lit.[12] 287 nm (ε 21)]; nmr ($CCl_4$) δ 0.94, 1.0, 1.38 (broad), 2.5, 3.25 (modified triplet).

Preparations in which the product azide was contaminated with excess amine were purified by chromatography through deactivated alumina or silica gel, or by vacuum distillation.

**2,4,4-Trimethyl-2-pentyl Azide.**—Similarly, 0.5 ml (0.84 g) of trifluoromethanesulfonyl anhydride was slowly added to 2 ml of a 6.25 *N* aqueous solution of $NaN_3$ over 5 ml of $CH_2Cl_2$ containing 0.496 g of 2,4,4-trimethyl-2-pentylamine and the mixture was stirred for 2 hr at 0°. The reaction mixture was treated as described above for *n*-hexyl azide and yielded 0.359 g (77.7%) of 2,4,4-trimethyl-2-pentyl azide: bp 40° (3.5 mm); ir 4.75

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$\mu$ ($N_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 289–290 nm ($\epsilon$ 18); nmr $\delta$ 1.03 (9), 1.30 (6), 1.49 (2).

**Registry No.**—Triflyl azide, 3855-45-6; *n*-hexyl azide, 6926-45-0; 2,4,4-trimethyl-2-pentyl azide, 35426-97-2.

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## A Convenient Synthesis of Homocubane-4-carboxylic Acid

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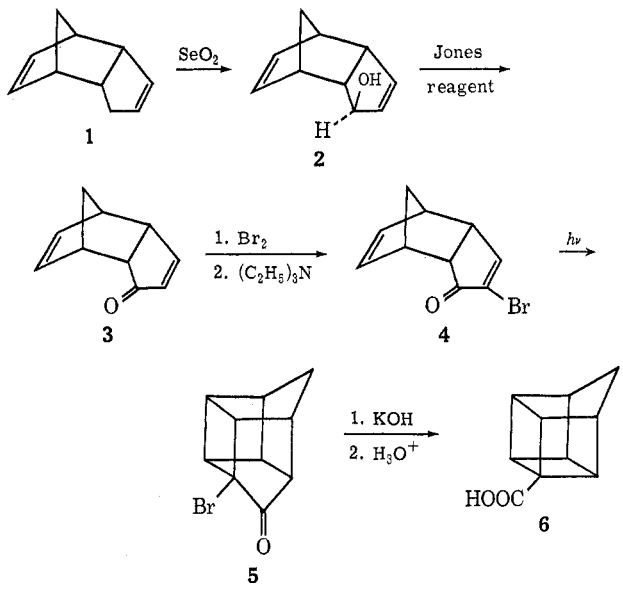
In connection with studies concerning mechanistic aspects of the $Ag^+$-catalyzed rearrangement of cubyl systems,[2] a number of various 4-substituted homocubanes (pentacyclo[4.3.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]nonanes) were required.[3] Since all of the desired compounds could be derived readily from that member of the series at the highest oxidation level, attention was given to the preparation of suitable quantities of homocubane-4-carboxylic acid (**6**). The original route to this compound reported in 1968 by Dunn, DiPasquo, and Hoover[4] began with relatively expensive 2-cyclopentenone and afforded **6** in less than 10% yield. We describe now a procedure which comprises only five readily executable steps, utilizes inexpensive dicyclopentadiene (**1**) as starting material, and results in at least 27% overall conversion to **6**.

Selenium dioxide oxidation of freshly distilled **1** according to the procedure of Woodward and Katz[5] led to the formation of allylic alcohol **2** in 63% yield. Efficient oxidation (75% yield) of this compound was achieved by treatment with Jones reagent.[6] Further studies indicated that **3** could be selectively brominated $\alpha$ to the carbonyl group by direct addition of




elemental bromine in carbon tetrachloride solution and subsequently dehydrobrominated with triethylamine. The halogenated ketone obtained in this manner (75% yield) was identical with an authentic sample of **4** prepared in unequivocal fashion.[4] Photocyclization of **4** and Favorskii-type ring contraction of **5**[4] complete the sequence.

### Experimental Section

*endo*-**3a,4,7,7a-Tetrahydro-4,7-methanoinden-1-one (3).**—A solution of 40 g (0.27 mol) of **2**[5] in 500 ml of acetone was cooled in an ice bath and titrated with a total of 170 ml of Jones reagent (*ca.* 0.2 *M*) prepared according to the method of Meinwald, *et al.*[7] The reaction mixture was added to 1 l. of brine and extracted with ether. The combined organic extracts were washed with water and dried. Evaporation of the solvent left an oily residue which solidified on standing. Recrystallization of the white solid from pentane gave 30 g (75%) of crystalline ketone, mp 80° (lit.[6] mp 80°).

*endo*-**2-Bromo-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (4).**—A solution of bromine (20.1 g, 0.126 mol) in 200 ml of carbon tetrachloride was added rapidly to a vigorously stirred solution of ketone **3** (18.3 g, 0.126 mol) in 500 ml of the same solvent. This was quickly followed by the addition of triethylamine (25 g, 0.25 mol) in 100 ml of carbon tetrachloride. The reaction mixture was warmed on a steam bath for 30 min and then stirred for a final 1.5 hr. The precipitate was separated by filtration and the filtrate was washed with water. The aqueous washings were extracted with ether and the combined organic layers were dried and evaporated. Short-path distillation of the residue afforded 21.5 g (75%) of **4** as a pale yellow oil, bp 95–100° (0.1 mm), which crystallized subsequently, mp 55–57° (lit.[4] mp 56–57°). The nmr spectrum of this material conformed to the reported spectrum of **4**.

**Registry No.**—**3**, 5530-96-1; **4**, 10481-35-3; **6**, 15844-05-0.

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