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°).

Acknowledgment. This work was supported by National Institutes of Health Grant No. N.S.-10203 from the National Institute of Neurological Diseases and Stroke.

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

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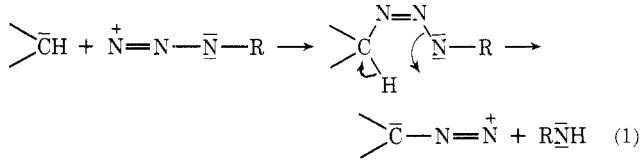
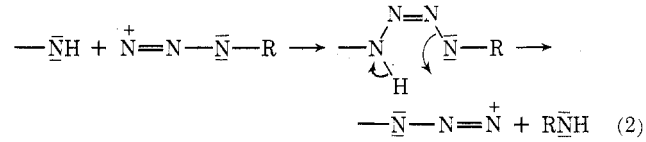
The *diazo transfer* reaction (eq 1), originally studied by Dimroth[1] and Curtius,[2] remained dormant until its epochal revival by Doering and De Puy in 1953.[3] Since that time, it has become a well-established route to α-diazocarbonyl compounds, largely through the extensive work of Regitz and his 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]



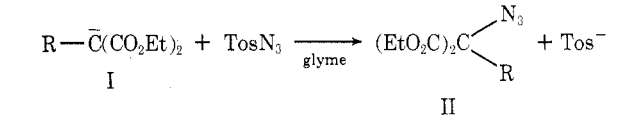
(1)



(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.

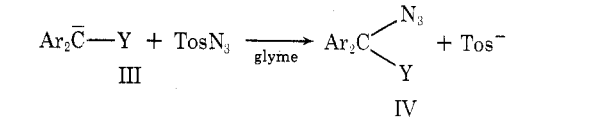
The reaction of the sodium salts of diethyl phenyl- and 7-cycloheptatrienylmalonate (Ia and Ib) with tosyl azide gave the corresponding azidomalonates (IIa and IIb) in 77 and 65% yields, respectively. The replacement of one



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

g, 77%) after evaporation of the solvent, ir (CCl_4) 2120 (N_3), 1750 1770 (C=O), 690 cm^{-1}.

The infrared spectrum of the product was identical with that of diethyl azidophenylmalonate prepared from diethyl bromophenylmalonate and sodium azide according to a published procedure.[18]

Diethyl Azido(7-cycloheptatrienyl)malonate (IIb). A procedure similar to that used in the synthesis of the azidophenylmalonate was employed, starting with 5.29 g (0.021 mol) of diethyl (7-cycloheptatrienyl)malonate.[19] The usual work-up procedure yielded 3.80 g (65%) of a yellow oil, ir (CCl_4) 2120, 1750, 1740, and 700 cm^{-1}.

The crude product was purified by chromatography on activated alumina and eluted with benzene–hexane (1:3), nmr (CCl_4) δ 1.30 (t, 6 H), 2.19 (t, 1 H), 4.20 (q, 4 H), 5.20, 6.15, 6.60 (m, 6 H).

9-Carbomethoxy-9-azidofluorene (IVa). The sodium salt of 9-carbomethoxyfluorene (2.80 g, 0.0125 mol) was prepared from reaction with sodium hydride as described above. To the brown solution of the anion was added dropwise a solution of 2.46 g (0.0125 mol) of tosyl azide in glyme at room temperature, and the reaction mixture was then heated under reflux for 2 hr. After having been cooled to room temperature, it was poured into ice water and extracted with ether. The dried ethereal extract was then evaporated *in vacuo* to give a pale yellow oil which crystallized on standing. Upon filtration and washing with petroleum ether, 1.90 g (57%) of colorless crystals of essentially pure product, mp 76–78°, were isolated, ir 2100 (N_3), 1740–1710 cm^{-1} (CO_2CH_3). An analytical sample was obtained by recrystallization from petroleum ether, mp 80–81°.

Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.86; H, 4.21; N, 15.68.

α-Azidodiphenylacetonitrile (IVb). The procedure was essentially identical with that described for IVa. The dark red oil obtained was refluxed with *petroleum ether* for 1 hr and the extract was decanted from the insoluble residue. Evaporation gave a red oil which was chromatographed on Florisil, using *petroleum ether* as eluent. A second chromatography of the second fraction gave 0.92 g (18%) of pure product, mp 40–42° (lit.[20] mp 41°), ir 2170 (CN), 2170 cm^{-1} (N_3).

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Registry No.—Ia, 28744-77-6; Ib, 51157-37-0; IIa, 51065-36-2; IIb, 51157-38-1; IIIa, 51065-38-4; IIIb, 51065-37-3; IVa, 51065-39-5; IVb, 51065-40-8; tosyl azide, 941-55-9.

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(16) Other products were formed during this reaction. With methyllithium as the base, a compound analyzing for $C_{15}H_{13}N_3$ was isolated. In the case of sodium hydride, an orange compound corresponding to $C_{28}H_{21}N_3$ was isolated in good yield. The structures of these two by-products remain unclear at this time.
(17) All melting points are uncorrected. Infrared spectra were recorded in solution (CCl_4) or potassium bromide pellets; nmr spectra were recorded as solutions in deuteriochloroform, using TMS as an internal standard.
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Cleavage of δ-Keto β,γ-Unsaturated Esters by 1,4-Diazabicyclo[2.2.2]octane

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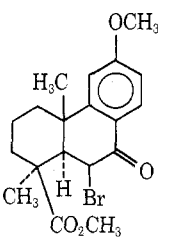
As a result of a continuing study into the improvement of the yield of lactone **2** from bromo ketone **1** by utilizing a variety of bases[4-6] we now wish to report that 1,4-diazabicyclo[2.2.2]octane (Dabco) is useful for the cleavage of δ-keto β,γ-unsaturated esters to their corresponding α,β-unsaturated ketones.



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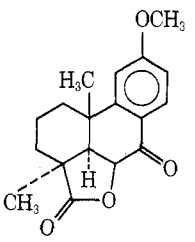

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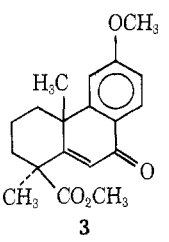

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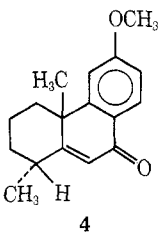

4

Bromo ketone **1** was reacted with 6 equiv of Dabco in 16 equiv of *o*-xylene at reflux (165°) for 6 hr. Fractional crystallization of the product mixture gave compound **4** in 80% yield and compound **2** in 10% yield. Compounds **2** and **4** were identical by ir, nmr, glc retention time, and mixture melting points with authentic samples.[4,5] Thus this reaction did produce some of the desired lactone **2** in contrast to the bases 1,5-diazabicyclo[4.3.0]nonene-5 (DBN)[4] and 1,5-diazabicyclo[5.4.0]undecene-5 (DBU).[5] However, the major component was the decarbmethoxylation product **4**. When the proposed intermediate **3** was treated with Dabco under the conditions previously described, a high (90%) yield of decarbmethoxylation product was obtained.

Since the bases DBN and DBU are *O*-alkyl cleavage reagents,[4,5] Dabco was allowed to react with esters **5**–**8** to determine if similar results could be obtained. The fact that no reaction occurred eliminates the possibility that Dabco is an *O*-alkyl cleavage reagent and indicates that this reagent cleaves δ-keto β,γ-unsaturated esters selectively.

The generality of Dabco as a reagent for cleaving δ-keto β,γ-unsaturated esters is demonstrated by the application