Anal. Calcd for $C_{20}H_{23}NO_3S_2$: C, 61.67; H, 5.95; N, 3.60. Found: C, 61.56; H, 5.98; N, 3.64.

Pyrolysis of 2-Phenylcyclohex-2-enyl-*N*-methyl-*N*-(*p*-toluenesulfonyl)sulfinamide. Injection of a 25% solution of the N-methyl adduct in CH_3OH directly into the gas chromatograph (injection port temperature 250 °C) gave (by area %) 6.4% 1-phenylcyclohexene, 3.6% biphenyl, and 90% diene.

The diene was isolated by preparative GLPC (20 ft × 3/8 in. stainless steel, 20% Carbowax 20M on 45/60 mesh Chromsorb W at 200 °C, t_r = 22 min (t_r(biphenyl) = 26.5 min, t_r (1-phenylcyclohexene) = 19 min, collected at liquid N_2 temperatures). The resulting oil was weighed and dissolved in cyclohexane: UV_{max} 279 nm (ε 7500).

Some biphenyl (230 nm) was present. Both 2-phenyl-1,3-cyclohexadiene (276 nm (ε 8140)) and 1-phenyl-1,3-cyclohexadiene (303 nm (ε 13 800)) are known.[14] Not more than 14% of the 1-phenyl isomer can be present in the isolated samples.

Both 1-phenylcyclohexene and biphenyl were identified by coinjection which authentic samples. Biphenyl was isolated and found to be identical (TLC, melting point, and mixture melting point) with an authentic sample.

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Registry No.—*p*-Toluenesulfonamide, 70-55-3; thionyl chloride, 7719-09-7; *N,N*-dichloro-*p*-toluenesulfonamide, 473-34-7; methanesulfonamide, 3144-09-0; *N*-(*p*-toluenesulfonyl)-2-phenyl-2-propenylsulfinamide, 64976-25-6; α-methyl-β-tritriostyrene, 64976-26-7; 1-phenyl-1-cyclohexene, 771-98-2; 2-phenylcyclohex-2-enyl-*N*-(*p*-toluenesulfonyl)sulfinamide, 64976-27-8; 2-phenylcyclohex-2-enyl-*N*-methyl-*N*-(*p*-toluenesulfonyl)sulfinamide, 64976-28-9; biphenyl, 92-52-4; 2-phenyl-1,3-cyclohexadiene, 15619-34-8; 1-phenyl-1,3-cyclohexadiene, 15619-32-6.

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Aliphatic Azoxy Compounds. 7. Unsymmetrical (Dialkoxymethyl)phenyldiazenes: Deoxygenation of an Azoxy Function[1]

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In an investigation of the reactivity of the biologically important distal carbon atom of a model azoxyalkane, we observed that **1a** was converted, in good yield, to phenyldimethoxymethyldiazene (**2a**).[2] We wanted to know if the reaction conditions permitted the incorporation of two different alkoxyl group nucleophiles into **2** or if alkoxyl group interchange (e.g., via addition to tautomer **3**[3]) would prevent this. In so doing we wanted to learn more about the scope of this reaction for the synthesis of compounds **2**, an unusual, and new, class of azo compound. Herein we report on the preparation, stability, and spectral properties of **2b–d**, results which apply in a practical way to the questions raised above.

The starting azoxy compound **1c** was prepared by the procedure used previously for **1a,b,d**.[2] Compounds **1b–d** were smoothly converted to liquids **2b–d** by treatment with triethylamine in methanol at 25 °C in the presence of a drying agent (see Scheme I). Conversion of **1** to **2** was 95–98% complete as determined by VPC; isolated yields of 49–58% of 98% pure **2** were obtained after silica gel chromatography. Diazene **2c** was prepared in comparable yield by alternate routes starting with **1a** in 1-propanol and using triethylamine or potassium hydroxide as bases. Diazene **2c** was stable for more than 1 day in refluxing 0.05 N aqueous methanolic potassium hydroxide solution, conditions expected to hydrolyze hydrazone **3** should it be formed in situ. In contrast, **2c** was quickly destroyed in 0.03 N hydrochloric acid at room temperature.

Scheme I

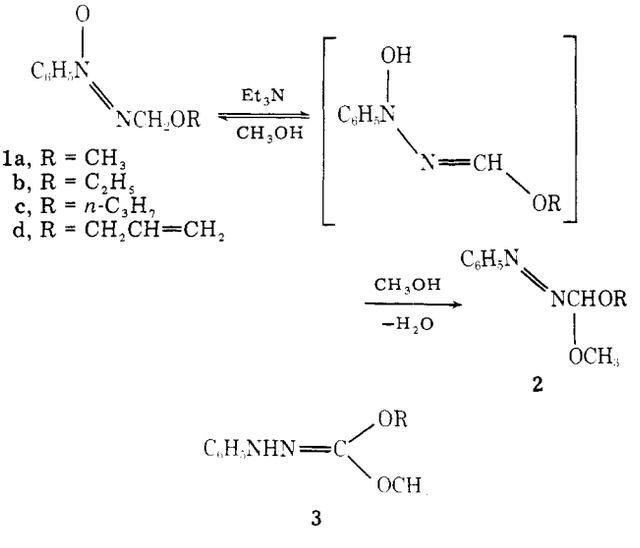

Table I. Spectral Features of (Dialkoxymethyl)phenyldiazenes 2[a]

Compd	Registry no.	R	^{1}H chemical shift, δ (Me_4Si) CH	OCH_3	α	β	γ	UV λ_{max} (EtOH), nm (log ε)
2b[b]	65102-03-6	$-CH_{2\alpha}CH_{3\beta}$	5.09	3.48	3.80[c]	1.19		269 (3.92), 215 (3.95)
2c[d]	65102-04-7	$-CH_{2\alpha}CH_{2\beta}CH_{3\gamma}$	5.02	3.53	3.72[c]	1.63	0.95	268 (3.96), 215 (4.01)
2d[b]	65102-05-8	$-CH_{2\alpha}CH_{\beta}{=}CH_{2\gamma}$	5.18	3.55	4.38	5.0–5.4	5.6–6.2	269 (3.92), 214 (4.02)

[a] All compounds showed NMR absorptions at δ 7.7 for *o*-Ph and at δ 7.5 for *m*- and *p*-Ph protons; IR absorptions included those at 1520 (medium, $\nu_{N=N}$), 1120 and 1060 cm^{-1} (strong, ν_{CO} acetal). [b] NMR solvent: acetone-d_6. [c] Diastereotopic splitting of the expected multiplet was observed. [d] NMR solvent: CCl_4.

The structures of **2b–d** are based on their elemental analyses and the spectral data gathered in Table I. The spectral features which distinguish the diazenes **2** from a possible (tautomeric) hydrazone structure are (1) the chemical shift of the methylidyne H, δ 4.9–5.2 (vs. δ >6.5 for the usually broad phenylhydrazone NH[4]), (2) the value of the UV extinction coefficient (ε) for the 260–280-nm absorption of phenylalkyldiazenes near 10 000[5] (vs. 18 000–20 000 for the similar absorption of phenylhydrazones[6]), and (3) the absence of NH stretch in the IR spectra of **2** (vs. ν_{NH} of 3300–3450 cm^{-1} for hydrazones[6]).

The conversion of **1** to **2**, analogous to the conversion of di(1-butyl)diazene oxide to 1-butyl-2-pentyldiazene by methyllithium,[7] joins the growing list of selective transformations which can be effected at both distal[2] and proximal[8] carbon atoms of azoxyalkanes.

Experimental Section

General. For instruments used see the Experimental Section of ref 2. VPC analyses were performed using the following aluminum tubing columns: A, 4 ft × 0.25 in. 10% SE-30 on Chromosorb W (AW and DMCS); B, 6 ft × 0.25 in. 5% silicone oil Dow 710 on Chromosorb W (AW and DMCS); C, 6 ft × 0.125 in. 5% UCW 98 on Diatoport S. Dialkyldiazene oxides are animal carcinogens. However, phenylhydroxymethyldiazene 1-oxide (**1**, R = H) produced no tumors in rats at dose levels which with dimethyldiazene oxide produced tumors with 100% frequency.[9]

(*Z*)-Phenylpropoxymethyldiazene 1-Oxide (1c). The title compound was prepared in 85% yield using the silver carbonate procedure described in ref 2. Preparative VPC (column A) provided an analytical sample: NMR ($CDCl_3$) δ 8.12 (m, 2 H, *o*-Ph), 7.4 (m, 3 H, *m*- and *p*-Ph), 5.15 (s, 2 H, distal CH_2), 3.62 (t, 2 H, OCH_2), 1.71 (m, 2 H, CCH_2), 0.97 (t. 3 H, CH_3); IR (neat) 1490, 1425, 1355, and 1325 cm^{-1}; UV λ_{max} (95% C_2H_5OH) 247 nm (ε 10 500). Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27. Found: C, 61.61; H, 6.98.

(*E*)-(Methoxyethoxymethyl)phenyldiazene (2b).[10] A mixture of 0.560 g (3.1 mmol) of **1b**, 0.50 g of triethylamine, 0.50 g of magnesium sulfate, and 0.25 g of calcium sulfate in 7 mL of methanol was stirred 1 day at room temperature. After filtration and concentration in vacuo the resulting red oil was chromatographed over 30 g of silica gel. Elution with benzene gave 0.30 g (50%) of 95% pure **2b** as a red oil. Preparative VPC using column B gave an analytical sample. Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.74. Found: C, 62.00; H, 7.38.

(*E*)-(Methoxypropoxymethyl)phenyldiazene (2c). This compound was prepared from **1c** and methanol in 58% yield, 98% pure, by the method described for **2b**. Preparative VPC on column A gave an analytical sample. Alternately, **2c** was prepared in similar yield from **1a** and 1-propanol using triethylamine as base and from **1a**, 1-propanol, and 0.2 mol equiv of 1 N KOH. Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74. Found: C, 63.22; H, 7.57.

(*E*)-(Methoxy-2-propenoxymethyl)phenyldiazene (2d). This compound was prepared from **1d** in 49% yield by the method used to make **2b**. Preparative VPC using column B gave an analytical sample. Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84. Found: C, 63.88; H, 6.78.

Stability Studies. A solution of 0.10 g of **2c** in 0.5 mL of 0.1 N aqueous hydrochloric acid and 1.0 mL of methanol was stirred at room temperature. VPC analysis (column C) after 1 h showed no trace of **2c**.

VPC analysis (column C) of a solution of **2c** in 0.5 mL of methanolic 0.1 N KOH and 0.5 mL of water showed no loss of **2c** after 1 day at reflux and 10% loss of **2c** after 6 days at reflux.

Registry No.—**1b**, 57496-83-0; **1c**, 65102-06-9; **1d**, 57496-85-2; methanol, 67-56-1.

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An Improved Method for the Synthesis of Stabilized Primary Enamines and Imines

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Primary β-enamino carbonyl compounds are interesting as potential intermediates in the synthesis of natural and synthetic compounds possessing biological activity. They are rendered especially versatile by their reactivity at both nitrogen and the α carbon, with the possibility existing of systematically directing reaction at either site.[1] Established syntheses of these compounds proceed from the corresponding β-dicarbonyl compound using ammonia[2] or a synthetic equivalent of ammonia[3] to form the enamine. Although these methods are useful, both lack generality when dealing with multifunctional compounds which are sensitive to the strongly basic and nucleophilic reagents required by each. Thus, the Dieckmann–Prelog method[2] (direct treatment with ammonia) is time consuming and apparently limited to structurally simple β-keto esters.[3] The Takaya method,[3] while more general in scope, requires in its second step the use of sodium ethoxide in refluxing ethanol, conditions which are often destructive to other moieties in a potential substrate, particularly exchangeable esters.

This note describes a new method for effecting this transformation which uses a markedly less nucleophilic reagent and proceeds under acid catalysis. *N*-Trimethylsilyliminotri-

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