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Photochemical Generation of Stable *o*-Xylylene Derivatives by the Electrocyclic Ring Opening of Some Polycyclic Benzocyclobutene Derivatives

Robert D. Miller,*[1a] Jaroslav Kolc,[1b] and Josef Michl[1b]

Contribution from the IBM Research Laboratory, San Jose, California 95193, and the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

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Abstract: Simple substituted derivatives of *o*-xylylene **1** which are stable and characterizable in fluid solution at room temperature in the absence of oxygen are generated by the irradiation of the polycyclic benzocyclobutenes **2b**, **3b**, and **12** in 3-methylpentane glass (77 K). The photochemical ring opening requires rigid media and may involve a successive absorption of two photons by the starting materials. The similarity of the UV and emission spectra of **5b**, in which the chromophore is restricted to coplanarity, with those of the parent *o*-xylylene **1** suggests that **1** is close to planar. The regular vibrational progression of ca. 1500 cm^{-1} seen in the absorption spectrum of **5b** indicates a general increase in the lengths of the C=C bonds in the excited state. While **5b** shows no tendency to thermally reclose upon standing at room temperature, irradiation at 350 nm either in rigid media or in fluid solution leads to a rapid nonstereospecific reclosure to regenerate the benzocyclobutene derivatives **2b** and **3b**.

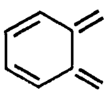
Introduction

The nature of the electronic states of *o*-xylylene (*o*-quinodimethane, **1**) coupled with the high chemical reactivity of the parent and its simple derivatives continues to attract considerable attention.[2,14] In the present paper, we report the preparation and characterization of some simple polycyclic derivatives of *o*-xylylene by photolysis of the corresponding benzocyclobutene derivatives. The cyclic substituents: (1) provide structural rigidity to facilitate spectral analysis, (2) prevent the thermal reclosure of the corresponding benzocyclobutene derivative by a symmetry preferred conrotatory process,[3] and (3) inhibit dimerization by sterically hindering both faces of the reactive *o*-xylylene moiety. The electrocyclic photochemical reactions employed are mechanistically intriguing in that they proceed in rigid but not in fluid solution and may involve a stepwise two-photon process.

Results

The unsaturated endo derivative **2a** was prepared as described by Nenitzescu.[4] Consistent with the assigned endo geometry was the observed doublet ($J = 3.5$ Hz) for the protons H_a in the NMR.[5] The saturated derivative **2b** was easily produced by hydrogenation of **2a** over PtO_2. The unsaturated exo derivative **3a**[6] was the major product of the in situ reaction of benzyne generated from *o*-bromofluorobenzene with norbornadiene. The NMR spectrum of **3a** showed the corresponding protons H_b at τ 6.88 (vs. 6.34 for H_a in **2a**) as a slightly broadened singlet. The saturated exo derivative **3b** was again produced by catalytic hydrogenation.

Preliminary indications that **2** and **3** are precursors to the rigid, strained *o*-xylylenes **5** come from thermolysis experiments. For example, gas-phase pyrolysis of either **2a** or **3a** leads to the isolation of the same tetracyclic adduct **4** in good yield.[7]



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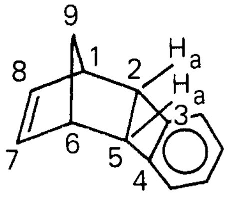
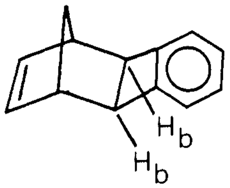


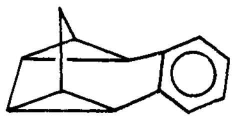
2a

2b -7,8-Dihydro



3a

3b -7,8-Dihydro



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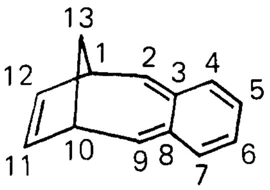


5a

5b -11,12-Dihydro

The production of **4** is most simply explained in terms of intramolecular trapping of the *o*-xylylene **5a**. In a similar fashion, the saturated endo derivative **2b** was quantitatively isomerized to the thermodynamically more stable **3b** upon pyrolysis presumably via **5b**. While it seemed clear from these results that the corresponding *o*-xylylenes were intermediates in the thermolysis, the extreme reaction conditions precluded identification or isolation before stabilization via intramolecular isomerization occurred. In an effort to produce the intermediates **5a,b** under milder conditions to allow identification and spectral characterization, the photochemistry of **2** and **3** was examined.

The initial photochemical results in fluid solution were somewhat disappointing. For example, the irradiation of either **2a** or **3a** at 254 nm for long periods of time caused the slow disappearance of starting material but failed to produce significant amounts of volatile products. More importantly, at no time during the irradiation could the presence of the cycloadduct **4** be detected by GLC. Similarly, analysis of the photolysis mixtures from either **2a** or **2b** failed to show any evidence of endo-exo isomerization to either **3a** or **3b**, respectively, as a diagnostic test for the formation of the corresponding *o*-xylylene derivative.

In contrast, a rigid solution of **2b** in 3-methylpentane at 77 K is 90% converted to a photoproduct upon irradiation with the same 254-nm source after only 30 min. When the irradiation is interrupted after about 80% conversion and the residual volatile products analyzed by NMR, none of the epimer **3b** is detected. The photochemical reaction can also be effected by a 214-nm source (Zn lamp). The same product is obtained from either **2a** or **2b**.[8] The UV absorption spectrum of the photoproduct is shown in Figure 1. It consists of a highly structured band in the region 310-420 nm where the starting materials do not absorb. The longest wavelength peak lies at 412 nm, and the most pronounced vibrational spacing is ca. 1500 cm^{-1}. The photoproduct also shows strong structured fluorescence in the region 410-540 nm (Figure 1) which is a fairly close mirror image of the 310-420 nm absorption band. The shortest wavelength peak lies at 417 nm. The excitation spectrum preserves its shape for various monitoring wavelengths between 410 and 540 nm and closely resembles the 310-420 nm absorption band. Thus, there is no doubt that the absorption and emission are due to the same species, and there is no evidence of additional products.

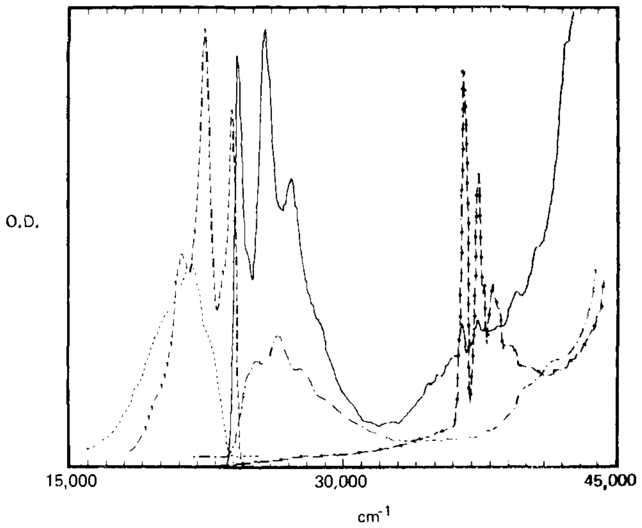
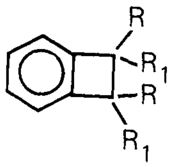


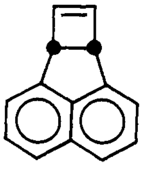
Figure 1. Absorption spectrum of **26** before irradiation (-•- -•-). After irradiation 0.5 h at 254 nm, absorption spectrum of **5b** ( ). Emission spectrum of **5b** (- -), not corrected for instrument response (arbitrary scale). Absorption spectrum of **1** (- - - -). Emission spectrum of **1** (- - - - -).

By analogy to the low-temperature photochemical behavior of a variety of polycyclic cyclobutenes such as **6-9** which all open to the corresponding butadienes,[1,9-11] the photoproduct from **2b** or **3b** is expected to be the tricyclic *o*-xylylene **5b**. This assignment is supported by the close similarity of the observed absorption and fluorescence spectra with those reported for **1** itself.[1] The better developed vibrational fine structure in the spectra of **5b** can be reasonably assigned to its increased rigidity and possibly also to the lack of steric interference between the inside hydrogen atoms on the methylene groups which may make absolute planarity difficult to achieve in **1**.



6a -R=R$_1$=H

6b -R=H, R$_1$=C$_6$H$_5$



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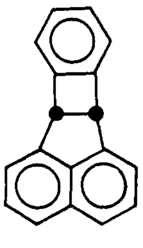

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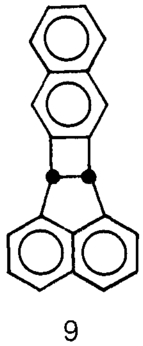
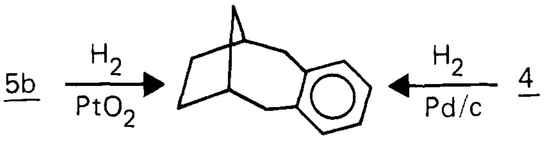


9

In the undegassed samples, warming to −100 °C and above results in rapid loss of the new product spectrum and in deposition of a colorless amorphous solid on the cell walls. The solid is soluble in 2-methyltetrahydrofuran, and its absorption spectrum shows only a broad featureless maximum near 270 nm. This material showed only broad NMR signals characteristic of a polymeric material. In addition to the absorptions in the aromatic and in the high field region (τ 7.0–9.1), a broad ill-defined resonance appeared at τ 5.2, possibly indicative of protons α to oxygen. No evidence for the formation of any dimeric product was produced.

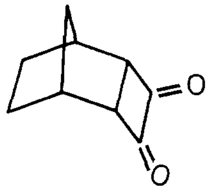
Surprisingly, when a solution of **5b** which had been thoroughly degassed prior to low-temperature irradiation was warmed to room temperature, a pale-yellow color remained and no polymer appeared. A visible spectrum of this solution run under nitrogen (25 °C) was almost identical with that previously observed in the rigid glass. When the tube was opened and a sample exposed to air, it rapidly decolorized with the precipitation of the amorphous colorless solid mentioned previously. A solution of **2b** (0.002 M) in 3-methylpentane was simultaneously irradiated (77 K) at 254 and 350 nm for 6 h. Warming to room temperature produced a clear, colorless solution which precipitated no polymer upon standing. Isolation of the volatile products from this solution and analysis by NMR showed that the only products were a mixture of **2b** (67%) and **3b** (33%). The volatile products were recovered in quantitative yield. In a similar fashion, when a degassed solution of **5b** in 3-methylpentane was irradiated at 30 °C using long wavelength light (350 nm) for 6 h, the pale-yellow color gradually faded to yield a colorless solution. As before, NMR analysis of the residue indicated a quantitative recovery of a mixture of **2b** (68%) and **3b** (32%). Control irradiation of a solution of **2b** under the same conditions failed to produce the exo isomer.

Further structural support was produced by catalytic hydrogenation of the *o*-xylylene derivative. When a solution of **5b** generated by irradiation of **2b** at 77 K and subsequent warming to room temperature was carefully hydrogenated over prereduced PtO_2 at room temperature, 3,4-benzobicyclo[4.2.1]nonane (**10**) was isolated (67%). The only other volatile material was a small amount of unphotolyzed starting material. The structure of **10** is supported by spectral and analytical data together with an unambiguous synthesis of the material by catalytic hydrogenation of **4**. It is interesting that the catalytic hydrogenation of **5b** occurs exclusively 1,4 at the termini of the *o*-xylylene moiety to regenerate the aromatic system in spite of the considerable steric shielding of these positions.



10

The photochemical generation of strained *o*-xylylene derivatives from benzocyclobutene derivatives fused to strained bicyclic derivatives seems reasonably general. For example, preliminary results on the low-temperature irradiation of the quinoxaline **12** produced from the diketone **11** showed the rapid generation of a purple photoproduct. Its absorption spectrum (400–610 nm) was highly structured with a pronounced vibrational spacing of 1600 cm^{-1}. It showed a mirror image fluorescence spectrum with an onset at ca. 600 nm. The similarity of this absorption and emission band shape with **5b** together with the red shift consistent with calculations strongly suggests that the structure of the purple photoproduct is that of **13**.



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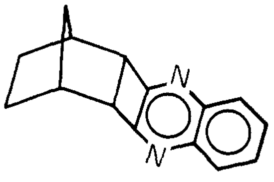

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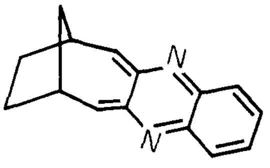

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Discussion

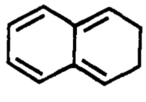
It is instructive to compare the spectra of **1** and **5b** (Figure 1). The 0–0 component of the $S_1 \leftarrow S_0$ electronic band lies somewhere between 412 and 417 nm for **5b** and in the vicinity of 415 nm in **1**. Each spectrum contains a prominent long progression in a ca. 1500 cm^{-1} vibration, slightly Franck-Condon forbidden. In **5b**, each individual component has a Franck-Condon allowed shape starting with a sharp peak, while in **1**, each individual component is broad, has a Franck-Condon forbidden envelope, and obviously contains many unresolved lines of similar intensity.

According to Dreiding models, the conjugated system in **5b** must be nearly perfectly planar, while complete coplanarity of the two exocyclic methylene groups in **1** can hardly be achieved as already pointed out above, and **1** in principle might prefer a completely noncoplanar geometry for one or both of its methylenes. However, it has been already suggested[2] that the observed strong fluorescence of **1** strongly indicates that it is nearly planar in both S_0 and S_1 states.

Since the requirement of planarity in **5b** hardly shifts the first electronic transition at all compared with **1**, it seems extremely unlikely that the geometries of the two species could be drastically different in either the S_0 or the S_1 states. We propose that in **5b** as in **1** the ca. 1500 cm^{-1} vibration corresponds to in-plane skeletal vibrations and appears as a result of fairly large differences in the lengths of C=C bonds in the S_0 and S_1 states, expected from calculated bond orders.[2] The broadness of the peaks of **1** relative to **5b** would then be caused by an unresolved progression in very low frequency vibration, perhaps a torsional vibration, appearing as a result of a difference in the degree to which the two interfering inside hydrogens on the exocyclic methylenes manage to avoid each other in the S_0 and S_1 states.

The amazing thermal stability of the polycyclic *o*-xylylene relative to **1** and other simple substituted derivatives can be understood as a consequence of steric hindrance to dimerization and the product strain developed in the symmetry preferred conrotatory closure.[3] An additional feature possibly related to the stability of **5b** is its inability to readily rearomatize via 1,5-sigmatropic migration. In this respect, it has been shown in related systems that alkyl migration is much slower than hydrogen migration.[12] Furthermore, the stability of cyclic o-xylylenes has some precedent in the behavior of **14**[13] and **15**[14] which apparently show some stability in solution at room temperature.[15] It is also interesting to note that the considerable steric hindrance afforded by the bicyclic moiety does not prevent rapid oxygen initiated polymerization or copolymerization in fluid solution.

Photocyclization of **5b** is relatively inefficient at 254 nm. However, irradiation into the absorption band of the *o*-xylylene



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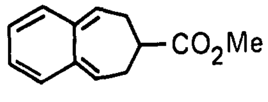

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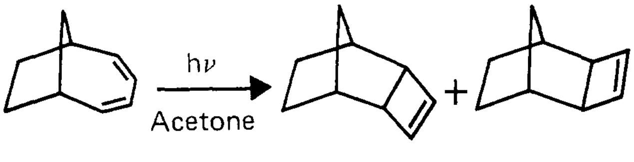
derivative using 350-nm light rapidly regenerates the starting material **2b** and the exo isomer **3b**. Under these conditions, the same mixture of (68:32) is produced irrespective of whether the irradiation is conducted in a glass at 77 K or at room temperature in fluid solution. This further assures that the species generated at low temperature is stable at room temperature and demonstrates that there is no obvious matrix or temperature effect on the stereochemistry of the photochemical reclosure of **5b**. The lack of stereospecificity in the photocyclization of **5b** is reminiscent of the results reported for bicyclo[4.2.1]nona-2,4-diene (**16**)[16] which yields a mixture of **17** and **18** in a relative ratio of 60/40 upon acetone-sensitized irradiation.



16 17 18

The difference in the room-temperature vs. low-temperature behavior of **2b** and **3b** cannot realistically be ascribed to either rapid thermal or photochemical reclosure at room temperature. As described, **5b** is relatively stable at 25 °C in the absence of air and disappears only slowly without reforming either **2b** or **3b**. In fluid solutions, the irradiation of either **2b** or **3b** proceeds very slowly and produces only compounds of higher molecular weight. Reisolation of the C_{13} material from these photolyses produces no evidence of isomerization of the starting material. The retention of the stereochemical integrity of the benzocyclobutene derivatives suggests that the rapid photochemical reclosure of **5b** is not the problem in the irradiations performed at room temperature. The temperature effect is most likely due to the two-photon nature of the photochemical process[17] as observed previously for similar molecules.[10,18] In this mechanism, the first photon converts the starting material into its unreactive S_1 and T_1 states, both short lived in fluid media. Return to S_0 is the only important subsequent event. In rigid media, T_1 is long lived, allowing a significant concentration to form, and absorption of a second photon by T_1 leads to ring opening. The operation of this mechanism can be demonstrated experimentally by a study of reaction rate as a function of light intensity and by double-beam studies. A mechanistic study will be the subject of another report.

Experimental Section

All NMR spectra were recorded on a Varian HA-100 instrument using tetramethylsilane as an internal standard. The low-resolution mass spectra were obtained on a Perkin-Elmer RMS-4 spectrometer. The GLC analyses were preformed on a Hewlett-Packard 5750 analytical instrument with a flame ionization detector. The low-temperature irradiation and spectroscopy were performed in Suprasil cells 2 mm optical path, immersed in a quartz Dewar with suprasil windows, filled with filtered liquid nitrogen. The initial concentrations of **2b** and **3b** were such that the optical density at the wavelength of the first absorption band (ca. 275 nm) was approximately unity. Absorption spectra were measured on a Cary 17 spectrophotometer, fluorescence on a home-made instrument described elsewhere.[2a] Low-pressure mercury and zinc vapor lamps served as photochemical light sources for the spectroscopic studies. 3-Methylpentane (Phillips 66, pure grade) was refluxed with and distilled from sodium-potassium alloy. The preparative scale irradiations were performed using a Southern New England Ultraviolet Co. Rayonet RPR-100 photochemical reactor employing either 25 nm low-pressure Hg or 350 nm Blacklite lamps.

***endo*-3,4-Benzotricyclo[4.2.1.0$^{2.5}$]non-7-ene (2a).** The tricyclic hydrocarbon **2a** was prepared in 54% yield by the method described by Nenitzescu and co-workers.[4] A small amount of yellow impurity was removed by chromatography on neutral alumina (Activity I) eluting with pentane: ^{1}H NMR τ (CCl_4) 3.15 (m, 4 H), 4.45 (t, J = 2Hz, 2 H), 6.34 (d, J = 3.5 Hz, 2 H), 7.1 (m, 2 H), and 8.2 (ABq, J = 8 Hz, 2 H); mass spectroscopic molecular weight 168.

***endo*-3,4-Benzotricyclo[4.2.1.0$^{2.5}$]nonane (2b).** The saturated hydrocarbon **2b** was prepared in quantitative yield by hydrogenation of **2a** in pentane over PtO_2: ^{1}H NMR τ (CCl_4) 6.43 (m, 2 H), 7.6 (m, 2 H), 8.31 (br s, 2 H), 8.58–9.13 (m, 4 H); mass spectroscopic molecular weight 170.

***exo*-3,4-Benzotricyclo[4.2.1.0$^{2.5}$]non-7-ene (3a).** The exo derivative **3a** was prepared by the procedure described by Simmons[6] using the following quantities: 21.15 g (0.23 mol) of distilled norbornadiene, 21.15 g (0.12 mol) of *o*-bromofluorbenzene, 2.96 g (0.12 mol) of clean magnesium, and 110 ml of dry THF. The desired hydrocarbon was obtained by chromatography on 20% silver nitrate impregnated silica gel with pentane as the eluent (25 g of adsorbent/1 g of hydrocarbon mixture): ^{1}H NMR τ (CCl_4) 3.0 (m, 4 H), 3.87 (t, J = 2 Hz, 2 H), 6.88 (s, 2 H), 7.23 (m, 2 H), and 8.9 (ABq, J = 9 Hz, 2 H); mass spectroscopic molecular weight 168.

***exo*-3,4-Benzotricyclo[4.2.1.0$^{2.5}$]nonane (3b).** **3b** was prepared in quantitative yield by hydrogenation as previously described for **2b.** ^{1}H NMR τ (CCl_4), 6.92 (s, 2 H), 7.78 (m, 2 H), 8.31 (br s, 2 H), and 8.58–9.13 (m, 4 H); mass spectroscopic molecular weight 170.

Preparation of the Quinoxaline Derivative 12 of Tricyclo[4.2.1.0$^{2.5}$]nonane-3,4-dione (11). A. A 100-m*l* flask was charged with 882 mg (3 mmol) of*endo*-bis(3,4-trimethylsiloxy)tricylo[4.2.1.0$^{2.5}$]non-3-ene[19] and 50 ml of carbon tetrachloride. Then 15 ml of a 0.2 M solution of bromine in carbon tetrachloride was addd at −15 °C under N_2. After 2 h at −15 °C, the solvent was removed on the rotary evaporator to yield the unstable diketone **10** as a tacky orange solid. ^{1}H NMR ($CDCl_3$) τ 6.6 (t, J = 3 Hz, 2 H), 7.13 (m, 2 H), 8.3 (m, 2 H), and 8.53 (m, 4 H); IR (CCl_4) 2920, 2850, 1780, 1750, 1180, and 1090 cm^{-1}.

B. The crude orange diketone was treated without further purification with 357 mg of freshly sublimed *o*-phenylenediamine (3.3 mmol) in 50 ml of THF and refluxed under N_2 for 4 h. The solvent was removed on the rotary evaporator and the residue chromatographed on 50 g of silica gel using benzene–3% acetone to yield 550 mg (82%) of a tannish solid which was >95 pure **12.** The material could be further purified by recrystallization from hexane and subsequent sublimation: mp 104–6 °C; ^{1}H NMR ($CDCl_3$) τ 3.36 (m, 2 H), 3.72 (m, 2 H), 6.60 (m, 2 H), 7.73 (m, 2 H), 8.48 (m, 4 H), and 9.22 (d, J = 8 Hz, 1 H). Anal. ($C_{13}H_{14}N_2$): C, H, and N.

Irradiation of 2a at 30 °C. A Vycor tube was charged with 50 mg (0.3 mmol) of **2a** dissolved in 10 ml of spectrograde hexane. The solution was freeze–thaw degassed to <1 μm and sealed. The tube was then irradiated at 254 nm for 5 h. The solvent was removed from the yellow solution. NMR and GLC analysis of the concentrate (6 ft × ⅛ in. 10% UCW98 on 60/80 Chromosorb W, T-150 °C) showed the starting material as the only volatile material present.

Irradiation of 2b at 30 °C. A Vycor tube was charged with 50 mg of **2b** (0.29 mmol) dissolved in 10 ml of spectrograde hexane. After degassing, the tube was sealed and irradiated at 254 nm as above for 7 h. The solvent was removed on a rotary evaporator and NMR analysis showed only the starting material. None of the corresponding exo isomer was detected in the photolysis mixture.

Irradiation of 2b at 77 K. 2b (16.0 mg, 0.095 mmol) was dissolved in 32 ml of spectrograde 3-methylpentane and placed in a Vycor tube. The solution was vigorously degassed with a N_2 stream and sealed. The tube was irradiated (254 nm) with eight lamps at 77 K for 6 h, after which it was allowed to warm slowly to room temperature. Under these conditions no polymer coating was visible and the solution remained a faint yellow. The tube was opened under N_2 and a sample removed. When the solvent was removed a white polymeric precipitate appeared in the flask. A sample of the photolysis mixture was carefully diluted 1/10 with degassed 3-methylpentane and the UV spectrum recorded; λ 408, 385, 368, 350 (sh) nm. This compared very well with that of the *o*-xylylene **5b** measured at 77 K. The visible absorption of this sample decayed with the appearance of the above polymer until after 3 h the sample was colorless. At the same time, there was no observable increase in the absorption due to unphotolyzed starting material.

Low-Temperature Irradiation of 2b at 254 and 350 nm. A. A Vycor tube was charged with 11.0 mg of **2b** and 32 ml of 3-methylpentane. After degassing, it was simultaneously irradiated at 77 K for 6 h using eight 254-nm and seven 350-nm lamps. Upon warmup to room temperature, the solution was colorless. NMR analysis of the concerned photolysis mixture showed a mixture of **2b** (63%) and **3b** (37%).

B. 2b (12.0 mg) was dissolved in 32 ml of 3-methylpentane in a Vycor tube, degassed, and sealed. The tube was irradiated for 3 h (eight 254-nm lamps) at 77 K and allowed to warm to room temperature. It was then irradiated at 30 °C for an additional 4.5 h (eight 350-nm lamps). At this point, the solution was colorless and free of polymer. NMR analysis of the mixture indicated 62% **2b** and 38% **3b.** In a control experiment 13.1 mg of **2b** in 32 ml of degassed 3-methylpentane was irradiated for 6.5 h (15 350-nm lamps). Removal of the solvent yielded 10.1 mg of the starting material (77%) and none of the exo isomer **3b.**

Trapping of 5b by Hydrogenation. A Vycor tube was charged with 15 mg of **2b** and 30 ml of 3-methylpentane. The tube was vigorously degassed with nitrogen, sealed, and irradiated at 254 nm (77 K) for 7 h. The solution was allowed to warm to −10 °C and rapidly transferred under nitrogen to a hydrogenation vessel containing 50 mg of prereduced PtO_2. The hydrogen pressure was maintained by a balloon for 15 h while stirring at 25 °C. The catalyst was filtered and GLC analysis (6 ft × ¼ in. glass, 10% SE-30 on 60/80 Gas Chromosorb Q, T-150 °C) showed the presence of starting material and dihydroderivative **10** in the ratio of 1:2. GLC collection on the above column (160 °C) yielded 9 mg of the bicyclic derivative **10** which was spectrally and chromatographically identical with a sample prepared by an independent route.

3,4-Benzobicyclo[4.2.1]nonane (10). 3,4-Benzotetracyclo[4.3.0.0^{2,8}.0^{5,7}]nonane (**4**) (53 mg) was dissolved in pentane and hydrogenated (1 atm) for 1.5 h over Pd/C. Filtration and removal of the solvent yielded **10** in quantitative yield: mp 43.5–45 °C; ^{1}H NMR τ (CCl_4) 3.15 (br s, 4 H), 7.23 (d, J = 4.5 Hz), 7.57 (m, 2 H), 8.03 (m, 1 H), 8.38 (d, J = 12 Hz, 1 H), 8.39–9.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 142.4, 133, 127, 47, 46, 37, and 30; IR (neat) 3050, 3010, 2920, 2900, 1490, 1465, 1445, 1440, and 735 cm^{-}; mass spectroscopic molecular weight 172. Anal. ($C_{13}H_{16}$): C, H.

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Communications to the Editor

A Polyamide Support for Oligonucleotide Synthesis

Sir:

Despite substantial success in the peptide field,[1] solid phase methods have achieved little in oligodeoxyribonucleotide synthesis.[2] Yields in internucleotide bond-forming reactions have often been so low that after three or four cycles the desired oligonucleotide is no longer even the major product. In part we attribute this relative failure to the widespread use of polystyrene and other nonpolar supports in these polar reactions. Recently we described a new, more polar polymeric support which gave improved results in both peptide synthesis[3,4] and protein sequencing[5] applications. We now show, by efficient stepwise synthesis[6] of d(pT$_6$-C) and d(pC-A-G-T-G-A-T) sequences required as primers for use in mRNA structure determination, that the new resin is also effective in the oligonucleotide field.

The preparation of the cross-linked polydimethylacrylamide resin has been reported previously.[3,4] It swells to about ten times its dry bed volume in pyridine, *N,N*-dimethylformamide, and other polar solvents. The amino-groups of β-alanine residues (0.4 mequiv g^{-1}), present as *tert*-butoxycarbonyl derivatives, serve as anchoring points. To obtain a suitable reversible linkage of the first nucleotide to the support, the β-hydroxythio ether, $HO(CH_2)_2S{\cdot}C_6H_4{\cdot}(CH_2)_2COOC_6Cl_5$ (I) was synthesized by standard methods[7] and attached to the support by one cycle of the activated ester peptide synthesis program.[3] This involves acidic removal of *tert*-butoxycarbonyl groups, neutralization, and reaction with a five-fold excess of I. Completion of the reaction was assayed qualitatively by the ninhydrin test.[8] The substituted support is now in effect a polymeric protecting group for the 5′-phosphate of a growing oligonucleotide chain, similar to those already used successfully in solution.[9-11] Cleavage of oligonucleotides from the support is effected by *N*-chlorosuccinimide oxidation of the sulfide to the sulfone followed by β-elimination under mildly alkaline conditions.

In a preliminary experiment the dinucleotide d(pT-T) was synthesized. A diester approach analogous to that developed by Khorana was used.[12] Pyridinium 3′-*O*-acetylthymidine-