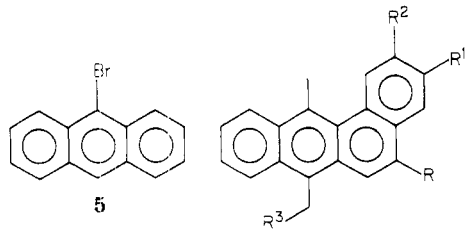
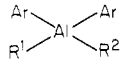
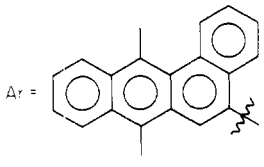


5

2, R = Br; $R^1 = R^2 = R^3 = H$
3a, R = $R^1 = R^2 = R^3 = H$
3b, R = ^2H; $R^1 = R^2 = R^3 = H$
4a, R = AlH_3^-; $R^1 = R^2 = R^3 = H$
4b, R = $Al^2H_3^-$; $R^1 = R^2 = R^3 = H$
6a, R = Al(H)(O^2H); $R^1 = R^2 = R^3 = H$
6b, R = Al(^2H)(OH); $R^1 = R^2 = R^3 = H$
7a, R = $R^1 = H$; $R^2 = F$; $R^3 = Cl$
7b, R = $R^2 = H$; $R^1 = F$; $R^3 = Cl$
7c, R = F; $R^1 = R^2 = H$; $R^3 = Cl$
7d, R = $R^2 = H$; $R^1 = OCH_3$; $R^3 = Cl$



4c, $R^1 = R^2 = H$
6c, $R^1 = OH(^2HO)$; $R^2 = H$
4d, $R^1 = H$; $R^2 = AR$



[a]anthracenes **7a–d** afforded site specifically monodeuterated compounds at the 7-methyl position. The reaction was insensitive to workup conditions, likely owing to direct displacement of halogen or reduction of an intermediate benzyl carbonium ion.

It thus appears that hydrogenolysis with $LiAlH_4$ of aryl halides proceeds via organoaluminums in addition to proposed four-membered cyclic transition-state intermediates. On the other hand, benzylic chlorides undergo hydrogenolysis exclusively by direct displacement of halogen by hydride.

Experimental Section

All melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. Ultraviolet and infrared spectra were recorded on Beckman UV-5260 and IR-4230 instruments. ^1H NMR spectra were determined on a Varian A-60A or Brucker 90-MHz instrument. 5-Bromo-7,12-dimethylbenz[a]anthracene (**2**) and 2-fluoro- (**7a**), 3-fluoro- (**7b**), 5-fluoro- (**7c**), and 3-methoxy- (**7d**) 7-(chloromethyl)-12-methylbenz[a]anthracene were prepared by known methods. Mass spectra were run with a Hewlett-Packard Model 5985 system. The quantity of site specifically introduced deuterium in DMBA was determined by mass spectrometry and nuclear magnetic resonance (90 MHz).

Hydrogenolysis of Aryl Halides (2 and 5). $LiAlH_4$ or $LiAl^2H_4$ (140 mg, 40 μmol) was suspended in dry THF (5.0 mL) and refluxed for 5 min. 5-Br-DMBA (13.3 mg, 40 μmol) in THF (3.0 mL) was added, and the mixture was refluxed for 24 h and cooled to room temperature. The excess $LiAlH_4$ or $LiAl^2H_4$ was decomposed by addition of either H_2O or ^2H_2O. Ether (20 mL) was added and the mixture vigorously stirred. The ether layer was separated, dried over sodium sulfate, and evaporated, furnishing crude DMBA (or deuterated DMBA). Subsequent purification by TLC (silica gel) and high-pressure liquid chromatography over Whatman Partisil PXS 10/25 ODS column (length = 25 cm; diameter = 4.6 mm) furnished pure samples which were analyzed for deuterium incorporation by mass spectrometry and 90-MHz NMR.

Hydrogenolysis of 7-(Chloromethyl)-12-methylbenz[a]anthracene Derivatives 7a to 7d. To a vigorously stirred suspension of $LiAl^2H_4$ (2 mmol) in ether (150 mL) under N_2 was added dropwise a solution of the respective 7-chloromethyl derivative (1 mmol) in dry THF (10 mL). After 1 h the excess $LiAl^2H_4$ was destroyed by addition of saturated ammonium chloride solution. The ether layer was dried over sodium sulfate and evaporated, furnishing a yellow gum which on subsequent column chromatography over silica gel (hexane–benzene, 1:1) furnished pure 7-methyl-deuterated DMBA derivatives characterized by examination of their NMR spectra.

Acknowledgment. Financial assistance from Public Health Service Grant No. CA-21371 from the National Cancer Institute and Environmental Protection Agency Grant No. R-805337 is gratefully acknowledged. We thank Dr. L. K. Wong, Department of Pharmacology, The Ohio State University, for mass spectral analyses. We thank Professor M. S. Newman of The Ohio State University for a gift of 5-Br-DMBA.

Registry No. 2, 34698-71-0; **3b**, 73873-01-5; **5**, 1564-64-3; **7a**, 73873-02-6; **7d**, 66240-01-5.

Mechanisms of Decomposition of the Ene Adducts of Some 1,3-Cyclohexadienes to Benzene or Tetralin and Dihydroenophile

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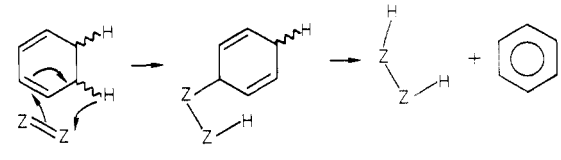
The Alder ene reaction can usually be run under mild conditions, especially when more active enophiles are used.[1] By contrast, it is unusual for either the reverse process[1,2] (retro-ene reaction) or other thermal breakdown of an ene adduct to occur at temperatures much below 200 °C, though there are some exceptions to this, e.g., the concerted decarboxylations of β-oxo acids and related compounds.[3,4] A common factor to several isolated reports of other ene adduct decompositions that occurred at moderate temperatures was a 1,3-cyclohexadiene structure for the adduct precursor.[5] As the decompositions in these cases usually resulted in aromatization and resemble the facile tetracanoethylene (TCNE) or quinone-mediated aromatizations of 1,4-cyclohexadienes,[6] it is not completely surprising that decomposition should occur, (see eq 1 for the overall



(1)

(1) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
(2) (a) R. T. Arnold and P. Veeravagu, *J. Am. Chem. Soc.*, **82**, 5411 (1960); (b) H. Kwart, J. Slutsky, and S. F. Sarner, *ibid.*, **95**, 5242 (1973).
(3) (a) F. H. Westheimer and W. A. Jones, *J. Am. Chem. Soc.* **63**, 3283 (1941); (b) J. A. King, *ibid.*, **69**, 2738 (1947).
(4) (a) The ene reaction of SO_2 and alkenes to give allylic sulfinic acid also appears to be readily reversible[4b] as is that of *N*-sulfinyl sulfonamides to give allylic sulfinamides.[4c] A few other ene reactions are also reversible at moderate temperatures,[1,2a] but there is no particular pattern to these. (b) D. Masilamni and M. M. Rogic, *J. Am. Chem. Soc.*, **100**, 4634 (1978); (c) J. Hori, S. P. Singer, and K. B. Sharpless, *J. Org. Chem.*, **43**, 1456 (1978).
(5) (a) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **27**, 1947 (1962); (b) A. Van der Gen, J. Lakeman, M. A. M. P. Gras, and H. O. Huisman, *Tetrahedron*, **20**, 2521 (1964); (c) A. L. Andrews, R. C. Fort, and P. W. Lequesne, *J. Org. Chem.*, **36**, 83 (1971); (d) B. M. Jacobson, *J. Am. Chem. Soc.*, **95**, 2579 (1973).
(6) For TCNE: B. M. Jacobson, *J. Am. Chem. Soc.*, **102**, 886 (1980), and references therein. For quinones: P. Müller, *Helv. Chim. Acta.*, **56**, 1243 (1973), and references therein.

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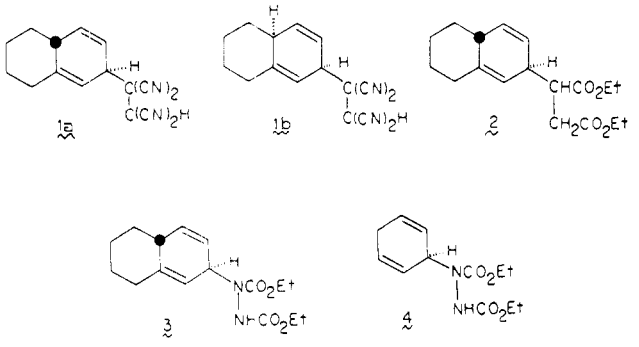
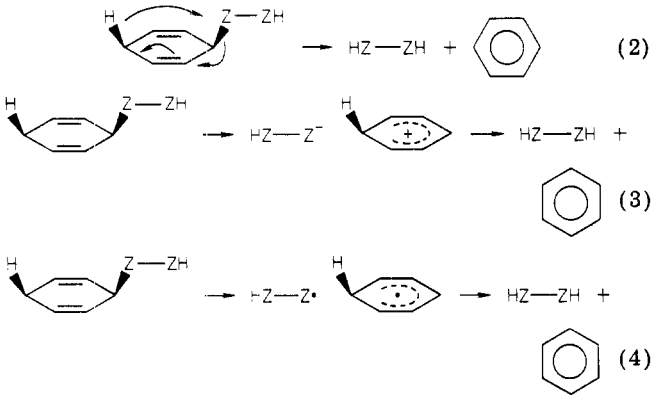
Chart I. Adducts Examined



process in the general case), but the facility of the reaction can be quite remarkable.[5c,5d] The question thus arises as to what structural or mechanistic features provide for this and whether any of these facile reactions take a concerted path, what might be termed an iso retro-ene reaction ($_{\sigma}2 + {}_{\pi}2 + {}_{\sigma}2$), eq 2, analogous to the few facile retro-ene



reactions known. Other mechanisms for the second step of eq 1 are easily formulated, a heterolytic reaction (eq 3) and a simple homolytic one (eq 4) as well as chain variants of the latter. Huisman proposed an ionic pathway for the decomposition of the ene adduct of diethyl azodicarboxylate (DAZD)[7] and 7-dehydrocholesteryl acetate[5] but no strong evidence was brought forward. A Pd/H_2 catalyzed decomposition of the adduct of DAZD and 1,3-cyclohexadiene has also been noted.[8] We have examined the decompositions of several 1,3-cyclohexadiene derived ene adducts (1–4, Chart I) and found a definite variation in mechanism with the structure of the adduct, but no good evidence for a concerted process in any case and arguments against it in two.

Results and Discussion

The TCNE adduct **1a** was exceedingly labile, decomposing cleanly to tetralin and tetracyanoethane in a first-order manner. As it was tempting to suspect concerted decomposition as in eq 2, compound **1b** was prepared for comparison. In the latter, the trans arrangement of the tetracyanoethyl group and the departing hydrogen mandate a stepwise process (or a least rule out an intramolecular concerted one). However, **1a** and **1b** were found to decompose at quite comparable rates. Further, the rate constant was strongly dependent on solvent (Table I), with

Table I. Variation in Decomposition Rates of 1a and 1b with Solvent Polarity at 35.5 °C

adduct	solvent	rate constant × 10^6 s^{-1}	solvent Z[a]	solvent dielectric constant[b]
1a	ether	1.5[c]		4.2
1a	acetone	41[d]	65.7	20.7
1a	ethanol	170[d]	79.6	24.3
1a	acetone/D_2O, 75:25 v/v	270[d]	82.1	20.7
1b	acetone	36[c,d]	65.7	20.7
1b	dimethylformamide	210[c]	68.5	36.7
1b	acetone/D_2O, 75:25 v/v	460[d]	82.1	
1b	acetone/D_2O, 65:35 v/v	1300[c]	84.3	

[a] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958). [b] C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965). [c] By ampule method. [d] By NMR method.

marked enhancement in both protic and aprotic polar solvents. A large increase in the rate of reaction of a neutral material when solvent polarity increases is a standard symptom of a heterolytic path.[9] Moreover, deprotonation of the adducts by base prevented the decomposition.[10] Heterolytic breakage of an already ionized adduct would require production of a 1,2-dianion, so a drop in rate is consistent with a heterolytic breakdown of the neutral adducts. Both expected fragment ions are strongly resonance stabilized (tetracyanoethane has a p*K*a of 3.6).[11] Initial concentrations of **1** were varied over a sixfold range with no noticeable effect on the rate constant. There is no sign of interconversion of **1a** and **1b** during the decomposition, though a few percent would easily escape notice in the NMR spectrum. A small contribution from a concerted reaction in a nonpolar solvent cannot be entirely excluded by our evidence, but we see no need to invoke it.

The diethyl fumarate adduct **2** was relatively stable, with even extremely slow decomposition (approximate rate constant 6×10^{-7} s^{-1} at 207 °C in chlorobenzene) achieved only above 200 °C. At those temperatures, more products than just tetralin and diethyl succinate were formed. NMR data indicated that some aromatization without cleavage of C–C bonds was a competing process. Decomposition could be induced by heating to 100 °C in the presence of dibenzoyl peroxide (DBPO). This result certainly indicates the feasibility of a free-radical pathway, but the higher temperature reaction was not investigated further because of its slowness and the multiplicity of products.

The DAZD derived adducts **3** and **4** were of intermediate stability with reference to **1** and **2**. They decomposed in a variety of solvents very cleanly at 119 °C (for **3**) or 144 °C (for **4**) to give 1,2-dicarbethoxyhydrazine and the corresponding aromatic residue. However, both adducts were very badly behaved kinetically. Although first-order plots were occassionally linear, most reactions were not of any simple order and many showed induction periods or initial periods of very slow reaction. Rapid decomposition could be induced by heating with DBPO, but no apparent effects were observed when azobis(isobutyronitrile), hydro-

(7) DAZD is suggested as the most convenient acronym for diethyl azodicarboxylate because the other term occasionally used, DEAD, can also be taken for diethyl acetylenedicarboxylate. DAZD also has a parallel in its derivation to the commonly accepted form TCNE for tetracyanoethylene.

(8) B. Franzus and J. H. Surridge, *J. Org. Chem.*, **27**, 1951 (1962).

(9) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(10) Prolonged exposure to base did result in decomposition of the adducts, but to ill-defined products rather than tetralin and tetracyanoethane.

(11) W. J. Middleton, R. E. Heckert, E. L. Little, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

Table II. Variation in Initial Decomposition Rate of 4 with Solvent Polarity at 144 °C

solvent	rate constant[a] $\times 10^5$ min^{-1}	solvent dielectric constant[b] at 25 °C
chlorobenzene	1.3 ± 0.7[c]	5.6
acetone	7 ± 2[d]	20.7
methanol	80 ± 20[d]	32.6
methanol/D_2O, 80:20 v/v	140 ± 20[d]	

[a] Uncertainties given are the ranges of triplicate or more runs. [b] C. Reichardt, *Angew Chem., Int. Ed. Engl.*, 4, 29 (1965). [c] By ampule method. [d] By NMR method.

quinone, 2,6-di-*tert*-butyl-4-methylphenol, or acetic acid were added to aliquot samples.[12] Exposure to air slowed some reactions but did not do so consistently. Distilling some of the solvents in vacuo from ethylenediaminetetraacetic acid directly into the NMR tubes used for the reaction did have a marked effect (over tenfold rate differences) but was upward in some cases (acetone-d_6, CH_3OD) and downward in another (CD_3CN). In attempts to find a solvent in which the reaction would behave, chlorobenzene, ethyl ether, acetone, acetonitrile, ethanol, and methanol as well as acetone-d_6/D_2O and CH_3OD/D_2O mixtures were all tried, but all showed large variations from run to run (often 10-fold, but occasionally over 100-fold in rate difference). No obvious dependence on solvent polarity could be seen for the bulk of the reaction, although altogether there was a variation in rate of over four orders of magnitude with solvent. Varying the initial concentration of **3** or **4** up to sixfold had no apparent effect on the rate, but the lack of reproducibility makes any conclusion from this very dubious. Careful examination of the rate data showed that a very slow reaction of **3** and **4** was occurring during the induction periods, and this may be indicative of competing heterolytic breakdown, as this initial rate showed a solvent dependence for **4** (Table II). However, with the rather variable rates seen, this interpretation is very tentative for **4** and the results with **3** were too erratic for any sensible analysis to be made.

Although the data do not allow a precise mechanism to be assigned for the decompositions of all the adducts, certain conclusions nonetheless emerge. First, decomposition of **1a** and **1b** is clearly ionic, while the reactions of **2**–**4** probably are not. Second, even with the uncertainty in rates for **3** and **4**, there is a clear decrease in the lability of the adducts, with the order being **1** < **3** < **4** < **2**. The relative ease of decomposition of all save **2** is a reflection of the stability of the likely intermediates: cyclohexadienyl cations or radicals, tetracyanoethyl anion, and the 1,2-dicarbethoxylhydrazyl radical. The trend in reactivity as well as the (likely) change in mechanism are probably related. If the identity of Z is held constant, the radical pair of HZZ· plus cyclohexadienyl and the ion pair HZZ^- plus cyclohexadienyl cation are related by simple electron transfer. Little information appears to be available for the species where Z equals $C(CN)_2$, NCO_2Et, and $CHCO_2Et$, but it is reasonable to expect the electron affinities of these radicals to decrease in that order.[13] The ionic nature and greater rate for the reactions of **1a** and **1b** would then follow.

In acetone-d_6 it was noted that the decompositions of both **3** and **4** were accompanied by a certain amount of exchange with the solvent of the hydrogen lost by the ring and of the hydrogen on the carbamate nitrogen. There was an increase in the residual protium appearing in the solvent NMR signal as the decomposition proceeded, with the N–H exchange being faster than the decomposition rate but with a burst at the end of the induction or slow reaction period. The other departing hydrogen exchanged only upon reaction; i.e., the only exchange detectible by NMR in the starting material was in the N–H group. This pattern is further evidence for a multiplicity of decomposition pathways for **3** and **4**.

Experimental Section

Materials. All of the ene adducts used had been previously characterized.[5a,d,8,17] Solvents were reagent grade: ether, acetone, and dimethylformamide (Fisher Sientific), absolute ethanol (Commercial Solvent Corp.), acetone-d_6, acetonitrile-d_3, and CH_3OD (Norell Chemical Co.), chlorobenzene (Eastman), and D_2O (Calbiochem-Biorad). Dibenzoyl peroxide and *m*-dinitrobenzene (Fisher), hydroquinone (J. T. Baker), thiophenol (Aldrich), and 2,6-di-*tert*-butyl-4-methylphenol (Eastman) were all used as received.

NMR Kinetic Method. The samples were prepared as solutions of ene adduct (0.08 to 0.40 M at 25 °C) and *m*-dinitrobenzene (0.20 M as internal standard for integration and possible free-radical-trapping agent)[18] in a 1-mL volumetric flask. The sample was divided between two NMR tubes equipped with ground joints. The tubes were degassed by freeze–pump–thaw cycling (to $<10^{-3}$ mmHg) and sealed. For reactions of **1a** and **1b**, the tubes were placed in the probe of a T-60 NMR spectrometer thermostated at 35.3 °C. Integrals were taken periodically for a least two and usually three half-lives. Heating overnight in an oil bath at 100 °C provided for an infinity point. For reactions of **3** and **4**, the sealed NMR tubes were immersed in a thermostated oil bath and periodically removed with immediate ice cooling, and the NMR spectrum and integral were taken. For these reactions, the temperature of the oil bath was selected so that warm-up and cool-down periods (checked with a thermocouple in an oil-filled NMR tube) were a negligible portion of the half-life (typically well under 0.2%). At the completion of some runs, tetracyanoethane (for **1**) or 1,2-dicarbethoxyhydrazine were isolated for identification (by IR), as their NMR spectra were considered insufficiently definitive for this purpose. A few runs with the *m*-dinitrobenzene left out gave the same results as those with it (the unvarying area of the carbethoxy signals allowed their use as an internal integration standard).

Ampule Kinetic Method. For **2**, which required reaction temperatures that resulted in some charring when *m*-dinitrobenzene was present or otherwise gave poor NMR spectra, an ampule/VPC method was used. Ampules were also used as a check on the NMR method for **1**, **3**, and **4**. Results with **1a**, **1b**, and with **3** or **4** plus DBPO gave rate constants within 10% of those determined by the NMR method. However, in the absence of DBPO, **3** and **4** could not be examined reliably by this method because individual ampules in the same run showed grossly different induction periods. Solutions of the ene adduct (0.05 to 0.3 M) and *n*-decane or *tert*-butylbenzene (0.1 M as internal standard) were prepared in a 2- or 5-mL volumetric flask. For **1a** and **1b**, the flask was stoppered with a serum cap and immersed in a thermostated water bath. Periodically, 100 μL of the solution was removed by syringe and the reaction was quenched by addition to 1 mL of 10% NaOH. Hexane (0.4 mL) was added and

(12) Thiophenol reacted directly with **2**–**4** below the temperatures needed for their decompositions.

(13) Although the electron affinities of the radicals are not known, a small amount of information is available concerning the radical anions derived from the parents—TCNE and diethyl fumarate. TCNE has an E.A. of 2.0 eV[14] and the radical anion produced is stable in ethereal solvents.[15] Diethyl fumarate radical anion has been produced electrochemically but dimerizes very rapidly.[16]

(14) L. E. Lyons and L. D. Palmer, *Chem. Phys. Lett.*, 442 (1973).

(15) M. T. Watts, M. L. Lu, R. C. Chen, and M. P. Easman, *J. Phys. Chem.*, 77, 2959 (1973).

(16) M. J. Hazelrigg, Jr., and A. J. Bard, *J. Electrochem. Soc.*, 122, 211 (1975).

(17) B. M. Jacobson, A. C. Feldstein, and J. I. Smallwood, *J. Org. Chem.*, 42, 2849 (1977).

(18) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, 68, 1686 (1946).

after shaking, samples of the organic layer were injected in the VPC (Varian Model 1200, FID detector, Linear Instruments Model 252A integrating recorder), using a 12 ft. × $^1/_8$ in. column of 8% Se-30 on 70/80 Anakrom ABS. All injections were done at least in duplicate. A blank showed that the NaOH/hexane treatment left the ratio of tetralin to standard unaffected. The FID response factors were the following: for tetralin–*tert*-butylbenzene, 1.00:1.07; for tetralin–decane, 1.00:1.11; for **2**–decane, 1.00:1.61; for **3**–decane, 1.00:2.34; for **4**–decane, 1.00:3.18. For compounds **2**–**4**, the solution in the volumetric flask was divided among 12 to 20 ampules, and the tubes were evacuated to 0.05 mmHg and sealed. They were then immersed in a thermostated oil bath and removed individually at intervals. VPC examination (3 ft × $^1/_8$ in. 10% SE-30 on 70/80 Anakrom ABS) required that the injection port be kept below 130 °C for **3** or 150 °C for **4** to prevent additional decomposition.

Reactions with Added Dibenzoyl Peroxide. Solutions were prepared as in the ampule method above, but 3 to 33 mg of the peroxide was added to the flask. After each ampule was opened, the contents were transferred to a test tube and stirred with 10 mg of $NaBH_4$ in 0.3 mL of 95% ethanol for 3 min to reduce any unreacted peroxide. Then 0.75 mL of aqueous 2 M NaCl and 0.3 mL of petroleum ether were added and the organic layer was examined by VPC. Blanks again showed no change in tetralin– or benzene–decane ratios from this treatment.

Reactions of 3 and 4 with Other Additives Present. Small amounts (up to 1.0 equiv) of azobis(isobutyronitrile), acetic acid, hydroquinone or 2,6-di-*tert*-butyl-4-methylphenol were added to an aliquot sample (NMR method) or several ampules. Unaltered samples were run in parallel. No apparent effect was observed. No effect was noticeable either upon rinsing the reaction tubes with ammonia or soaking in dichromate/H_2SO_4 before use. Air admitted to the NMR tubes (1 to 20 mmHg) before sealing appeared to decrease the rate somewhat for **4**, but plots were badly curved and the magnitude of the effect was not very reproducible.

Acknowledgment. We thank the Research Corporation for a Cottrell College Science Grant in support of this work.

Registry No. **1a**, 73873-09-3; **1b**, 73873-10-6; **2**, 73873-11-7; **3**, 73873-12-8; **4**, 73873-13-9; tetralin, 119-64-2; tetracyanoethane, 14778-29-1; dicarbethoxyhydrazine, 4114-28-7; benzene, 71-43-2.

A Convenient Method for Insertion of the 5′-Terminal Phosphate Group in the Triester Approach to Oligoribonucleotide Synthesis

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The phosphotriester approach has been examined by several workers[1-11] in an attempt to overcome some of the problems inherent in the phosphodiester method. However, only a few examples of the insertion of 5′-terminal phosphate residues in the phosphotriester approach to oligoribonucleotide synthesis[12] have been published. The native transfer ribonucleic acids (t-RNAs) contain a 5′-terminal phosphate. Consequently, the development of a convenient insertion of 5′-phosphate groups during the synthesis of oligoribonucleotides via the phosphotriester approach was required.

In this paper, we describe an efficient method for the synthesis of oligoribonucleotides bearing a 5′-terminal phosphate which uses 5-chloro-8-quinolyl phosphate (pqcl),[11f] 2,2′-dipyridyl diselenide [$(PySe)_2$],[13] and triphenylphosphine (Ph_3P).

The partially protected dinucleotides, dmtUt(qcl)Ut (**3a**) and dmtbzCtp(qcl)bzCt (**3b**) were prepared from 5′-*O*-dimethoxytrityl-2′-*O*-tetrahydropyranylnucleoside (**1**), 5-chloro-8-quinolyl phosphate, 2′-*O*-tetrahydropyranylnucleoside (**2**), and 8-quinolinesulfonyl chloride (QS),[11e] using the previous described procedure.[11e] In a similar manner, **3** and **2** were converted to a partially protected trinucleotide, dmbzCtp(qcl)bzCtp(qcl)bzAt (**4**) (Scheme I). These results are summarized in Table I. No evidence for undesirable 8-quinolinesulfonylated and 3′–3′ linkage products was detected in any of the coupling reactions. Subsequent removal of the dimethoxytrityl group from **3** and **4** to give **5** and **6**, respectively, was carried out with 2% *p*-toluenesulfonic acid solution.[11f]

The following is a typical procedure for the selective phosphorylation at the 5′-hydroxyl groups of **5** and **6** by means of 5-chloro-8-quinolyl phosphate in the presence of $(PySe)_2$ and Ph_3P. To a mixture of Utp(qcl)Ut (**5a**) (0.5 mmol), 5-chloro-8-quinolyl phosphate (0.75 mmol), and $(PySe)_2$ (5.25 mmol) in dry pyridine (5 mL) was added Ph_3P (5.25 mmol). The reaction mixture was stirred at room temperature for 12 h. The reaction was monitored by silica gel TLC. After completion of the reaction, the mixture was quenched with ice–water and extracted with methylene chloride, and the extract was back washed with triethylammonium bicarbonate (0.1 M, pH 7.5). The methylene chloride was evaporated in vacuo. The residue was dissolved in methylene chloride, applied to a silica gel column, and eluted with methylene chloride–methanol

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