# The Reaction of Nitriles with Solvated Electrons. III[1]

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**Abstract:** Study of the reaction of nitriles with solvated electrons demonstrated that reductive decyanation resulted from the interaction of primary, secondary, tertiary, and aromatic nitriles with solvated electrons generated from various sources. The reaction proceeds in high yields and is therefore attractive as a synthetic approach and as a new analytical procedure for the quantitative determination of tertiary nitriles. The reaction of 1,4-cyclohexanedicarbonitrile with solvated electrons seems to proceed *via* a 1,4 intradimerization.

A recent communication[2] revealed that the reaction of tertiary mononitriles with solvated electrons produces exclusively the corresponding hydrocarbon while vicinal tertiary dinitriles produces a mixture of the hydrocarbon and the tetrasubstituted olefin. The latter finding constitutes a new one-step synthesis of olefins[3] and of bicyclo compounds from easily accessible vicinal dinitriles.[4]

Essentially, the reaction comprises a reductive decyanation of a nitrile by solvated electrons[5] from (a) alkali metal and liquid ammonia[6] or lithium and an alkylamine, (b) an alkali metal and a polynuclear aromatic hydrocarbon,[7] or (c) electrolysis of an inorganic salt in an organic solvent, such as hexamethylphosphoramide[8] or an alkylamine.[9] However, systems consisting of an alkali metal in liquid ammonia or an alkylamine, usually a lower amine such as ethyl- or methylamine were preferred. The classical intense blue color[6] of solvated electrons was characteristic of these systems. Generally, the alkali metal was employed in an amount which was stoichiometrically equivalent or greater than that of the nitrile. Although the reaction proceeded rapidly and the product formed within a few seconds to several minutes, longer reaction periods generally were employed to assure completion of the reaction and an optimum product yield. Since inorganic cyanides are formed in these reactions, the customary precautions in handling cyanides were employed in product work-up.

Two methods were employed. With method a, a temperature at or just below the boiling point of the medium was employed. In general the reaction was exothermic, and a stepwise incremental addition of the nitrile to the medium, or *vice versa*, and/or cooling were employed to control the reaction temperature. Method b, utilizing biphenyl as the hydrocarbon, was advantageous because it could be carried out at room temperature and permitted convenient additions of a solution of solvated electrons to the desired nitrile.

## Results and Discussion

The existing analytical determination of organic halogen[10] by sodium biphenyl reagent coupled with the fact that these reductive decyanations proceeded rapidly, in high yield and with simultaneous ionizable cyanide generation, prompted us to determine the feasibility of the new reaction in analytical chemistry.

To date there is no known convenient analytical procedure for cyano group determination in nitriles even though cyanide ion determination can be easily accomplished by conventional means.[11]

There are various cumbersome classical methods[12] for

**Table I.** The Quantitative Determination of the Cyano Group in Tertiary Nitriles

| Nitrile | % CN Theoret | % CN Found[a] |
|---|---|---|
| Dehydroabietonitrile | 9.3 | 8.9 |
| 1,1′-Dicyanobicyclohexyl | 24.1 | 24.1 |
| Triphenylacetonitrile | 9.6 | 9.6 |
| 2,2′-Diphenylpropionitrile | 12.0 | 11.8 |
| 1,2-Dicyano-1,2-diphenylethane | 22.4 | 10.7 |
| Octanenitrile | 22.2 | 11.7 |

[a] As determined by the Liebig titrimetric method involving titration of the generated inorganic cyanide with silver nitrate. Duplicate and, in some cases, triplicate runs were made.

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[1] (a) Supported by the Pioneering Research Fund of Battelle Memorial Institute, Columbus Laboratories, to whom we are grateful for financial support. (b) Paper presented at the First Central Regional Meeting of the American Chemical Society in Akron, Ohio, May 10, 1968.

[2] P. G. Arapakos, *J. Amer. Chem. Soc.*, **89**, 6794 (1967).

[3] Work presently in progress to determine the product ratio of *cis/trans* tetrasubstituted olefins from the reaction of asymmetric vicinal dinitriles with solvated electrons may elucidate the mechanism of this reaction.

[4] (a) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Amer. Chem. Soc.*, **71**, 2661 (1949); (b) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

[5] E. J. Hart, "Solvated Electron," American Chemical Publications, Washington, D. C., 1965.

[6] (a) G. W. Watt, *Chem. Rev.*, **46**, 317 (1950); (b) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); (c) A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958).

[7] S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **88**, 4262 (1966).

[8] H. W. Sternberg, R. E. Markley, I. Wender, and D. M. Mahliner, *ibid.*, **89**, 186 (1967).

[9] (a) A. F. Fentiman, Jr., and R. H. Poirier, *Chem. Ind.* (London), 813 (1966); (b) R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, *J. Amer. Chem. Soc.*, **86**, 527 (1964).

[10] L. M. Liggett, *Anal. Chem.* **26**, 748 (1954).

[11] (a) L. F. Hamilton and S. G. Simpson, "Quantitative Chemical Analysis," The Macmillan Co., New York, N. Y., 1955, Chapter XV; (b) N. H. Furman, "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., Princeton, N. J., 1952, p 661.

[12] (a) P. J. Elving, and W. B. Liggett, *Ind. Eng. Chem., Anal. Ed.*, **14**, 449 (1942); (b) L. J. Lohr, T. E. Bonstein, and L. J. Franenfelder, *Anal. Chem.*, **25**, 1115 (1953); (c) P. K. Winter, *ibid.*, **15**, 571 (1943); (d) M. S. Arguss, G. W. Ayers, Jr., and H. Schindler, *Ind. Eng. Chem., Anal. Ed.*, **13**, 69 (1941).

Table II. Reaction of Nitriles with Solvated Electrons

| Compound | Method | Product(s)[a] | Yield, % |
|---|---|---|---|
| Triphenylacetonitrile | Na-$NH_3$ | Triphenylmethane | 90–96 |
| | Na-$(C_6H_5)_2$ | Triphenylmethane | 90–96 |
| Diphenylacetonitrile | Na-$NH_3$ | Diphenylmethane | 76 |
| | | Diphenylethylamine | 11 |
| | | Diphenylacetonitrile | 11 |
| Phenylacetonitrile | Na-$NH_3$ | Toluene | 90 |
| Benzonitrile | Na-$NH_3$ | Benzene | 60 |
| | | Benzonitrile | 40 |
| Tris(*p*-dimethylaminophenyl)acetonitrile | Na-$NH_3$ | Tris(*p*-dimethylaminophenyl)-methane | 93 |
| 1,4-Cyclohexanedicarbonitrile | Li-$EtNH_2$ | Cyclohexane | 49 |
| | | 2-Methylpentane | 37 |
| | | 3-Methylpentane | 14 |
| Tridecane nitrile | Li-$EtNH_2$ | Dodecane | 35 |
| | | Tridecylamine | 65 |

[a] These were separated and analyzed by vpc and by spectral means (ir, nmr, and MS-9 mass spectrometer). Where possible, direct comparison with authentic samples was made.

cleaving organic halides to produce ionizable halides that can then be determined titrimetrically. However, these procedures are not applicable to the cleavage of the carbon–nitrile bond since carbon dioxide, ammonia, and/or oxides of nitrogen are the major products from the cyano-group decompositions.

It was found that reductive decyanation of tertiary nitriles by sodium biphenyl, followed by the Liebig titration method[11] for quantitative cyanide determination, successfully comprised a new, rapid, and simple analytical procedure for cyano groups. Table I indicates the accuracy of the technique with tertiary, secondary, and primary nitriles. The results in Table I indicate quantitative recovery of cyanide for the tertiary nitriles within the experimental limit of the method, but no better than a 50% recovery for primary and secondary nitriles. The incomplete recovery of primary and secondary nitriles might be accounted for either by the reduction of the cyano group to the amine, or perhaps by some destructive disproportionation of the cyano group.

The reaction of nitriles with solvated electrons was further studied by screening the model compounds listed in Table II. As can be seen from the results, the tertiary nitriles proceed with exclusive reductive decyanation, whereas the primary and the secondary nitriles not only undergo cleavage of the carbon–nitrile bond but also reduction to the amine. However, this side reaction can apparently be avoided by the use of solvated electrons from other sources. For example, it was recently noted[13] that electrochemically generated solvated electrons cleaved the carbon–nitrile bond of primary and secondary nitriles without accompanying reduction to the amine. Work is presently in progress to assess the generality of this method for the quantitative cyano-group determination of all types of nitriles.

All products noted in Table II are the expected ones except for 2- and 3-methylpentane, which were obtained along with the anticipated cyclohexane from the reaction of 1,4-cyclohexanecarbonitrile with lithium in ethylamine (Scheme I). A possible explanation[14] for the unusual formation of these two isomeric hexanes is presented in Scheme I. A two-electron transfer to A could lead to the carbanion B and/or the free biradical C. A nucleophilic displacement at the cyano group or an intradimerization of the free diradical for B and C, respectively, would lead to bicyclo[2.2.0]hexane, D. This strained system containing two fused cyclobutanes undoubtedly has a strong tendency to cleave in the excess strong reducing medium of solvated electrons. Thus, cleavage between carbon 1 and 2 as well as 4 and 5 with subsequent partial protonation would lead to intermediate E, which would then lead to 2-methylpentane by a methyl-group migration followed by protonation. In turn, a concomitant or stepwise cleavage between carbon 2 and 3 and between carbon 4 and 5 and ultimate protonation would give rise to 3-methylpentane.

The identification[15] and separation of cyclohexane from

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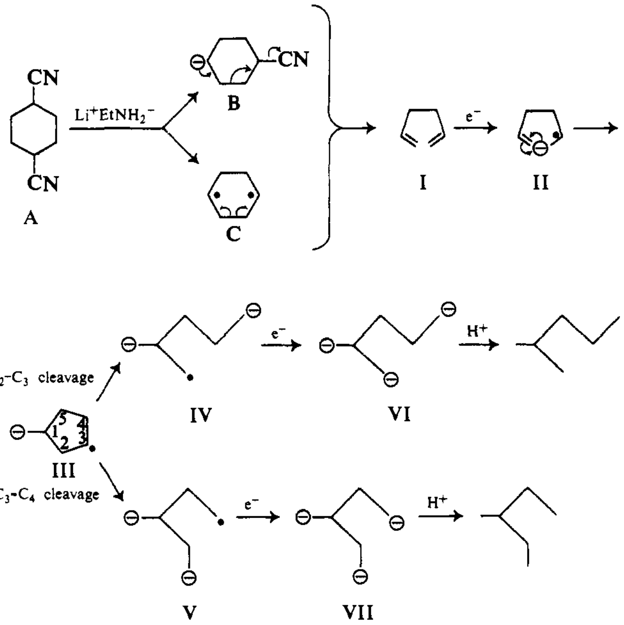
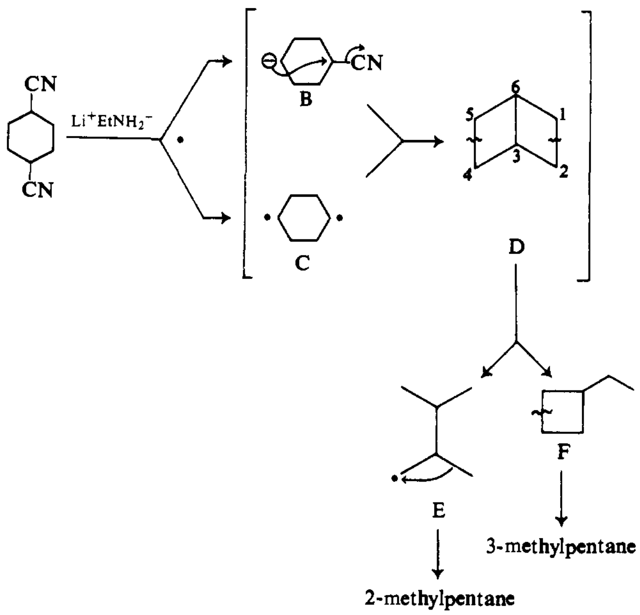
[13] P. G. Arapakos and M. K. Scott, *Tetrahedron Letters*, 1975 (1968).

[14] One of the referees suggested the following mechanism as a possible alternative to that shown in Scheme I.



[15] The mass spectra were obtained directly on the gas chromatograph effluent peaks by means of a coupled gas chromatograph–mass spectrometer system. The resulting spectra were identical with those of authentic samples.

Scheme I



2-methylpentane and 3-methylpentane was easily accomplished. However, the separation of the two hexane isomers became a major problem in itself by gas–liquid partition chromatography. The different chromatographic columns[16] tried at various temperatures failed to separate the methylpentanes in our hands. Ultimately, separation was achieved on a 400-ft capillary column[17] of squalene–hexadecane.

## Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer, and molecular weight was determined from MS-9 mass spectrometric data. Proton magnetic resonance spectra were obtained with Model A-60 using TMS as internal standard. Analytical gas chromatograms were obtained on a Varian Aerograph 202 with a thermal-conductivity detector and an Aerograph Hy-Fi (A-600-D) gas chromatograph equipped with a hydrogen-flame detector. Columns employed were 0.25 in. × 10 ft, 20% M TPA on 60–80 mesh Chromosorb W; 0.13 in. × 20 ft, 5% squalene on 70–80 ABS; 0.3 in. × 6 ft, stainless steel Poropak Q 60–100 mesh; $^1/_8$ in. × 6 ft, stainless steel Silinized Porasil 100–150 mesh, Type C; 0.02 in. × 400 ft capillary, 3% hexadecane–1.5% squalene. Melting points were taken on a Hershberg melting-point apparatus and are uncorrected.

**Materials.** Sodium biphenyl reagent (blue solution) was obtained from Hartman-Leddon Company, Inc. Benzene or toluene (Baker Analyzed Reagent) was dried and used as received. Silver nitrate was approximately 0.1 *N*, and was standardized. Ammonia and ethylamine were purchased from Matheson Coleman and Bell. Dehydroabietonitrile[18] was received from Hercules Powder Co., 2,2-diphenylpropionitrile, 1,2-dicyano- and 1,2-diphenylethane, diphenylacetonitrile, benzyl cyanide, benzonitrile, 1,4-dicyanocyclohexane, and tris(*p*-dimethylaminophenyl)acetonitrile were obtained from Aldrich; octane and tridecane nitrile were obtained from Eastman; and triphenylacetonitrile[19] and 1,1′-dicyanobicyclohexyl[4] were synthesized.

**Analytical Procedure.** A 100- to 200-mg nitrile sample was weighed into a 125-ml separatory funnel, and 10 to 20 ml of dry benzene (or toluene) was added to effect solution. To this mixture an excess of sodium biphenyl reagent (blue solution) was added. For most purposes 20 ml of sodium biphenyl reagent was sufficient. A brown color on mixing indicated that the reaction may have been incomplete, and more reagent was needed. The funnel was stoppered and shaken, venting carefully, since the reaction produced heat. The reaction was complete in 1 or 2 min.

A few drops of water were added to decompose the excess reagent; 25 ml of water was then added and the mixture was shaken gently. Vigorous shaking produced an unwanted emulsion. The aqueous layer was transferred to a beaker. Extraction of the organic layer was repeated twice with 25-ml portions of water. A few crystals of potassium iodide were added to the combined extracts and the resultant mixture was titrated with 0.1 *N* silver nitrate. The first appearance of silver iodide turbidity was taken as the end point. A blank was also determined with each sample.

**Reaction of Sodium–Liquid Ammonia Systems. Triphenylacetonitrile.** Under a nitrogen atmosphere, 4 g of sodium were added to 400–500 ml of liquid ammonia and stirred until a dark blue color persisted; this was followed by portionwise addition of 10 g of trityl nitrile. After 10–15 min further stirring, the resulting reaction mixture was poured into 200–300 ml of diethyl ether in a 4-l. beaker immersed in ice. Ice cubes were slowly added to the contents until the blue color was dissipated, and the ammonia was then allowed to boil off. The ether layer was separated from the aqueous residue, which was further extracted with five 100-ml portions of ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and evaporated to give 8.1–8.6 g (90–96%) of a white solid, mp 90–93°, which according to its infrared spectrum was free of any starting nitrile. A mixture melting point with an authentic sample of triphenyl methane, mp 92–95° showed no depression.

**Diphenylacetonitrile.** The same procedure as for triphenylacetonitrile was followed except that 2.5 g of sodium, 200–250 ml of liquid ammonia, and 5 g of diphenylacetonitrile were used. The combined ether extracts were analyzed by vapor phase chromatography on SE-52 3% on Chromosorb Q, programmed at 100–225° ballastic on 60% power, and flow rates of 24, 24, and 300 cc/min for helium, hydrogen, and air, respectively. The chromatogram of the separated products exhibited three peaks with retention times of 6.1, 8.8, and 10.1 min. These fractions (as identified by comparison with authentic samples) were diphenylmethane (76%), diphenylacetonitrile (11.1%), and diphenylethylamine (11.1%).

**Phenylacetonitrile.** The procedure followed was the same as that for triphenylacetonitrile except that 4 g of sodium, 400 ml of liquid ammonia, and 10 g of phenylacetonitrile were used. A gas–liquid chromatographic analysis of the combined ether extracts on a Polypak I at 225° revealed only one peak with a retention time of 1.4 min. This product, on comparison with an authentic sample, proved to be toluene.

**Benzonitrile.** The quantities of reactants and procedure was the same as that employed in reactions with phenylacetonitrile. Gas chromatography of the ether extracts on a 7% Apiezon "L" programmed at 50–200°, 6°/min, with a flow rate of 24 cc of helium/min showed two components with retention times of 3 and 12 min. These corresponded to benzene and benzonitrile, respectively.

**Tris(*p*-dimethylaminophenyl)acetonitrile.** The procedure and quantities of materials were the same as used for triphenylacetonitrile. The product was a white solid, 8.8 g (95%), mp 177–178° free of any starting nitrile as evidenced from its infrared spectrum. A mixture melting point with an authentic sample of tris(*p*-dimethylaminophenyl)methane, mp 178–179°,[20] showed no depression.

**Reaction of Sodium Biphenyl Reagent with Triphenylacetonitrile. 1.** To 7 g of melted triphenylacetonitrile, 200–250 ml of sodium biphenyl reagent was added slowly under a dry nitrogen atmosphere. The resulting mixture was stirred for periods varying from 20 min to 3 hr and then sufficient water was added to quench the reaction. After separation of the aqueous phase, the organic layer was freed from most of its solvents by evaporation under reduced pressure. The resulting mixture was then steam distilled until all the biphenyl was removed. The residue was dissolved in diethyl ether, dried over magnesium sulfate, filtered, and evaporated to give a brown solid which was then converted to a white solid, 5.6 g (90%), mp 91–20°, by chromatography on an alumina column with pentane as the eluting solvent. By spectroscopic and mixture

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[16] (a) 0.25 in. × 10 ft, 10% CW 20M TPA on 60–80 mesh Chromosorb W. (b) 0.3 in. × 6 ft stainless steel Poropak Q 60–100 mesh. (c) 0.25 in. × 25 ft, aluminum 25% squalene on Chromosorb P. (d) $^1/_8$ in. × 6 ft, stainless steel Silinized Porasil 100–150 mesh, Type C.

[17] We wish to thank Dr. K. W. Greenlee and Mr. J. E. Tabor of Chemical Samples, Columbus, Ohio, for their assistance in accomplishing this separation.

[18] The authors thank Dr. T. F. Sanderson of Hercules Powder Co. for the generous gift of dehydroabietonitrile.

[19] W. M. Budde and S. J. Potempa, *J. Amer. Chem. Soc.*, **74**, 258, (1952).

[20] F. K. Beilstein, "Handbuch der organischer Chemie," Vol. XIII, p 315.

melting point comparison, this solid was identified as triphenylmethane.

**2.** In a second experiment, everything was the same as the first procedure except that the nitrile was slowly added as a benzene solution to a stirred sodium biphenyl reagent under nitrogen at 25°. Triphenylmethane in comparable yield was again obtained.

**3.** In the third experiment, the triphenylacetonitrile was slowly added as a solid to the stirred sodium biphenyl reagent at 25°. Similar results to the above cases were again observed.

**Reaction of Lithium-Ethylamine. a. 1,4-Cyclohexanedicarbonitrile.** Under a nitrogen atmosphere and with stirring, 4 g of lithium was added to 500 ml of liquid ethylamine. When the appearance of the blue color persisted, 12 g of 1,4-cyclohexanedicarbonitrile were added portionwise over a 15-min period. The reaction mixture was stirred for 10 min more and then poured into a 2-l., round-bottomed flask connected to a 3 ft long fractionating column. A slow and careful addition of 300 ml of diethyl ether followed by 200 ml of cold water was made and then the ethylamine was slowly distilled off. The ether layer was separated from the resulting residue and its aqueous phase was further extracted with six 100-ml portions of ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and slowly concentrated to 30–40 ml, at an oil bath temperature of 40°, through a 4 ft long, vacuum-jacketed fractionating column. The mass spectra of the ether concentrate were obtained directly on the gas chromatograph effluent peaks by means of a coupled gas chromatograph–mass spectrometer system. The spectral analysis revealed the presence of cyclohexane and two isomeric noncyclic hexanes. The ethereal mixture was separated by gas–liquid partition chromatography on a 400-ft squalene–hexadecane capillary column at 21° with a flame ionization detector. The chromatogram obtained exhibited three peaks whose retention times were 21, 23, and 37 min. These three fractions were identified as 2-methylpentane (37%), 3-methylpentane (14%), and cyclohexane (49%), respectively, from a comparison with authentic samples.

**b. Tridecane Nitrile.** The procedure for 1,4-cyclohexanedicarbonitrile was again applied, except that 10 g of the nitrile was used. The combined extracts were dried over magnesium sulfate and then concentrated at 25° (25–30 mm). The resulting mixture was percolated through basic alumina, using pentane and methanol successively as the eluents. Dodecane (35%) and tridecylamine (65%) were obtained from the pentane and methanol effluents, respectively, as evidenced by a comparison with the physical constants of the authentic samples.

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# Photochemistry of Enolic Systems. IV.[1] Irradiation of Enol Trichloroacetates and a Dienol Trichloroacetate

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**Abstract:** The photolysis of enol trichloroacetates **1**, **3**, and **2** derived from 3-pentanone, 17β-acetoxy-5α-androstan-3-one (**9**) and cyclohexanone was investigated. The main products isolated in *t*-butyl alcohol were the α-trichloromethyl ketones **4** and **10** and an α-dichloromethylene ketone **7**, respectively, the latter being formed from the α-trichloromethyl ketone **6** by loss of hydrogen chloride. In addition, the steroidal enol trichloroacetate **3** yielded the dimeric enol tetrachlorosuccinate **11**. However, irradiation of **3** in cyclohexane or in isopropyl alcohol did not result in α-trichloromethyl ketone nor in its decomposition product. In cyclohexane three enol esters were isolated: **11**, the enol dichloroacetate **13**, and enol formate **14**, and in isopropyl alcohol the two former esters and a solvent addition product **15a**. Photolysis of steroidal dienol trichloroacetate **16** in both *t*-butyl alcohol and cyclohexane gave the trichloromethyl ketone **17** which was accompanied in the latter solvent by the α-dichloromethylene ketone **18**. The properties of the novel compounds are described and the relevant photochemical pathways are discussed.

We have extended our studies on the photolysis of enol esters[1] to include the enol trichloroacetates and a dienol trichloroacetate.

**Photolysis of Enol Trichloroacetates.** Enol trichloroacetates are novel compounds which are conveniently synthesized from ketones by the action of trichloroacetic anhydride in the presence of *p*-toluenesulfonic acid at 125–135°.[4] They absorb light at 190-mμ region like the corresponding enol acetates, but differ in having an additional absorption at *ca.* 220 mμ which appears as a shoulder on the higher intensity end absorption band. Their ε value at 253.7 mμ, the wavelength used in our experiments, is however similar (ε 30–60) to that of the corresponding enol acetates (ε 30–50).[5] For our irradiations we have chosen enol trichloroacetates **1**, **2**, and **3** derived from 3-pentanone, cyclohexanone, and 17β-acetoxy-5α-androstan-3-one (**9**). These three enol trichloroacetates were irradiated with a low-pressure immersion mercury lamp (emitting at 253.7 mμ) using *t*-butyl alcohol as a solvent.

Irradiation of the acyclic enol trichloroacetate **1** gave as

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(1) Part III: M. Gorodetsky and Y. Mazur, *Tetrahedron*, **22**, 3607 (1967).

(2) Taken in part from the Ph.D. thesis of J. L. submitted to the Feinberg Graduate School of the Weizmann Institute of Science, Rehovot.

(3) Department of Chemistry, University of Tel-Aviv, Israel, on leave of absence from Bar-Ilan University.

(4) J. Libman, M. Sprecher, and Y. Mazur, *Tetrahedron*, in press.

(5) A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).