Photoisomerization of *o*-Nitrobenzyl Compounds

AARON L. BLUHM, JOHN A. SOUSA, AND JULIUS WEINSTEIN

Pioneering Research Division, United States Army Natick Laboratories, Natick, Massachusetts

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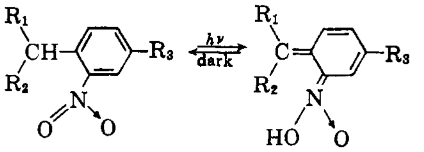
Kinetic data at several temperatures are reported for the dark fading reactions of the colored isomers formed by ultraviolet illumination of solutions of *o*-nitrobenzyl compounds in ethanol. Activation energies and entropies of activation are reported. Visible anionic spectra are shown to be similar to the photoisomer. The ultraviolet spectra are shown and discussed.

Recently it has been reported that photochromism in nitrobenzyl compounds requires only the presence of a nitro and $>$C–H group *ortho* to each other.[1,2] The color change shown by compounds of this type on irradiation is believed to be due to the formation of the tautomeric *aci*-nitro structure.[1,3,4]



The kinetics of the photoisomerization of 2-(2,4-dinitrobenzyl)pyridine and 2-(2-nitro-4-cyanobenzyl)-pyridine has been reported.[1] This paper presents a kinetic study of *o*-nitrobenzyl compounds I–IV listed in Table I, of the following type.

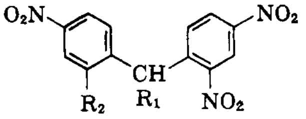


TABLE I

VALUES OF k, E_{exp}, AND ΔS^* FOR THE FADING REACTION IN ETHANOL

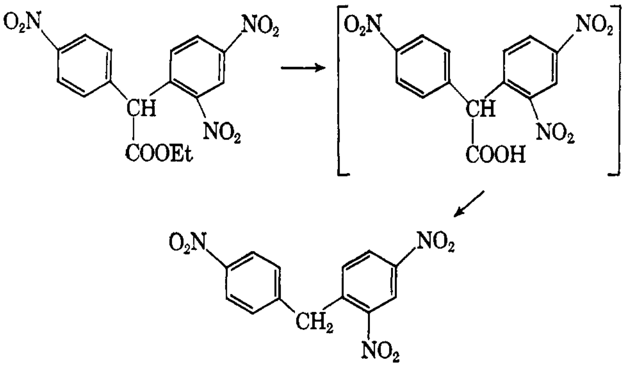
Compound	$k \times 10^5$ sec.$^{-1}$ (at $-50°$)	E_{exp}, kcal./mole^{-1}	ΔS^* *e.u.*
Methyl bis(2,4-dinitrophenyl)-acetate (I)	6.03	5.6 ± 0.1	−45
Ethyl bis(2,4-dinitrophenyl)-acetate (II)	0.785	5.4 ± 0.1	−50
2,4,4′-Trinitrodiphenylmethane (III)	0.695	5.4 ± 0.1	−50
2,4,2′,4′-Tetranitrodiphenyl-methane (IV)	2.84	5.5 ± 0.1	−47

Results and Discussion

Preparation of *o*-Nitrobenzyl Compounds.—When methyl bis(2,4-dinitrophenyl)acetate (I) was prepared as reported by Borsche[5] by the condensation of methyl 2,4-dinitrobromobenzene in the presence of sodium ethoxide in ethanol, a mixture of the methyl and ethyl esters resulted. The condensation carried out in methanolic sodium methoxide yielded pure I. Ethyl bis(2,4-dinitrophenyl)acetate was prepared by the nitration of ethyl diphenylacetate according to the method of Werner.[6]

Ethyl 2,4,4′-trinitrodiphenylacetate (VI) was obtained by condensation of methyl 4-nitrophenylacetate and 2,4-dinitrobromobenzene in the presence of sodium in ethanol. Contrary to expectations the same reaction carried out with sodium dissolved in methanol did not lead to the methyl ester, but furnished mainly starting material. In order to prepare the methyl ester, VI was hydrolyzed to the acid which, when treated with diazomethane, led to methyl 2,4,4′-trinitrodiphenylacetate (V).

2,4,4′-Trinitrodiphenylmethane and 2,4,2′,4′-tetranitrodiphenylmethane were prepared by the hydrolysis of VI and II, respectively, to the crude acids which were decarboxylated.



In order to hydrolyze the esters it was necessary first to dissolve them in hot concentrated sulfuric acid and then add water gradually to the heated solution. 2,4,4′-Trinitrodiphenylacetic acid and 2,4,2′,4′-tetranitrodiphenylacetic acid were not stable, readily losing carbon dioxide. The decarboxylation occurred readily when the acids were dissolved in ethanol at room temperature. A partial purification could, however, be effected by recrystallization from benzene, in which solvent the decarboxylation was slower, and in which the decarboxylated product was more soluble. The trinitro acid appeared to be slightly more stable than the tetranitro acid. The impure acids showed the characteristic COOH absorption bands in their infrared spectra. The nitrated diphenylmethanes (III and IV) have been prepared also by the nitration of diphenylmethanes.[7-9]

Attempts to prepare methyl 2,4-dinitrodiphenylacetate and methyl 2,4,2′-trinitrodiphenylacetate by the condensation of methyl 2,4-dinitrophenylacetate with bromobenzene or *o*-nitrobromobenzene with sodium in methanol failed. II could not be prepared

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(1) J. A. Sousa and J. Weinstein, *J. Org. Chem.*, **27**, 3155 (1962).

(2) G. Wettermark, *Nature*, **194**, 677 (1962).

(3) H. S. Mosher, C. Souers, and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960).

(4) R. Hardwick and H. S. Mosher, *ibid.*, **36**, 1402 (1962).

(5) W. Borsche, *Ber.*, **42**, 1310 (1909).

(6) A. Werner, *ibid.*, **39**, 1278 (1906).

(7) W. Staedel, *ibid.*, **23**, 2578 (1890).

(8) K. Matsumura, *J. Am. Chem. Soc.*, **51**, 816 (1929).

(9) J. D. Margerum, *et. al.*, *J. Phys. Chem.*, **66**, 2434 (1962).

by the reaction of methyl 2,4-dinitrodiphenylacetate and *p*-nitrobromobenzene.

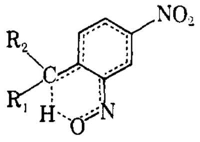
Color Phenomena.—When base is added to the colorless alcoholic solutions of these compounds an intense blue color is formed. Methyl and ethyl bis-(2,4-dinitrophenyl)acetate (I and II) are extremely sensitive to minute amounts of alkali, and scrupulous cleansing of glassware was necessary in order to avoid the slow formation of the blue color due to the apparent leaching of alkali from the glassware. In Fig. 1 the visible absorption spectra from the cold irradiation of the compounds are compared to the color formed by the addition of alkali to alcoholic solutions. The photochromic and base-produced spectra are similar. Margerum and co-workers[9] have reported the similarity of the anionic and photochromic spectra of various *o*-nitrobenzyl derivatives. In contrast, the spectra of irradiated neutral ethanolic solutions of *o*-nitrobenzylpyridines and the spectra of their anions are dissimilar.[1,4] Although it appears reasonable to attribute the blue color in ethanolic base to the anion, we have noted that either a blue or yellow color may be obtained by adjusting the ratio of water to ethanol.

Kinetics.—First-order kinetics was observed for the fading reactions of I–IV in ethanol as shown in Fig. 2. The kinetics for V and VI were not determined since the fading reaction was so rapid that acceptable measurements over a temperature range were not feasible. It was qualitatively observed that the addition of a small amount of alkali slowed the fading reaction. A similar pH effect has been noted in the case of 2-(2,4-dinitrobenzyl)pyridine.[10]

When solutions of 2,4,2′,4′-tetranitrodiphenylmethane were exposed to radiation in preliminary flash photolysis experiments at room temperature, reproducible results were not obtained due to the occurrence of decomposition. Apparently, the product formed accelerated the rate of color fading. However, there was no indication of decomposition under the conditions in which the reported kinetic measurements were made. Figure 3 shows the relationship of log k values and $1/T$ for the fading reactions of I–IV in absolute ethanol. Compounds I and II show two photochromic absorption bands, and the values of k measured by the change in absorbance as a function of time at $\lambda_{\max}$ of each band were the same, indicating that both bands are related to the same phenomenon.

Table I lists the values of k at $-50°$, the Arrhenius activation energies, and the calculated entropies of activation. Activation energies and entropies of activation are very close in value and are similar to those observed for the benzylpyridines.[1] The mechanism of fading is, therefore, probably the same for all these compounds.

The large decrease in entropy observed for the formation of the activated complex indicates that the structure in the activated state is probably more rigid than in the ground state. It has been proposed[1] that



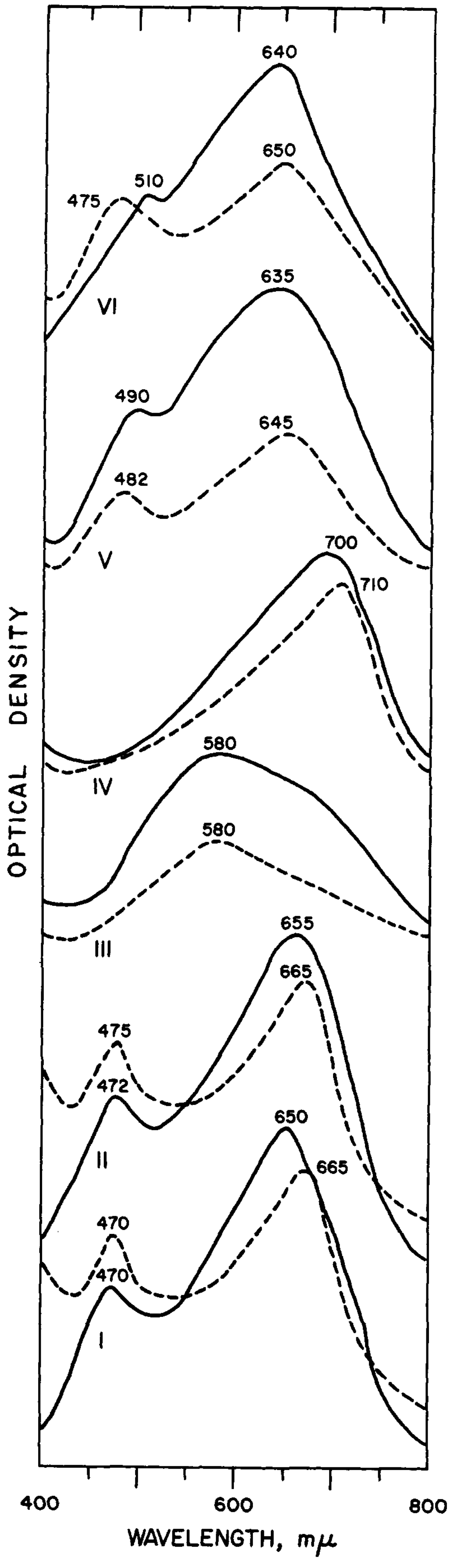


Fig. 1.—Visible absorption spectra of the irradiated cold solutions of the nitrobenzyls compared with the color obtained by adding alkali to the solutions at room temperature: dashed line, irradiated ethanol solutions at −103.5°; solid line, one drop 0.01 *N* potassium hydroxide added to the solutions at room temperature.

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(10) G. Wettermark, *J. Am. Chem. Soc.*, **84**, 3658 (1962).

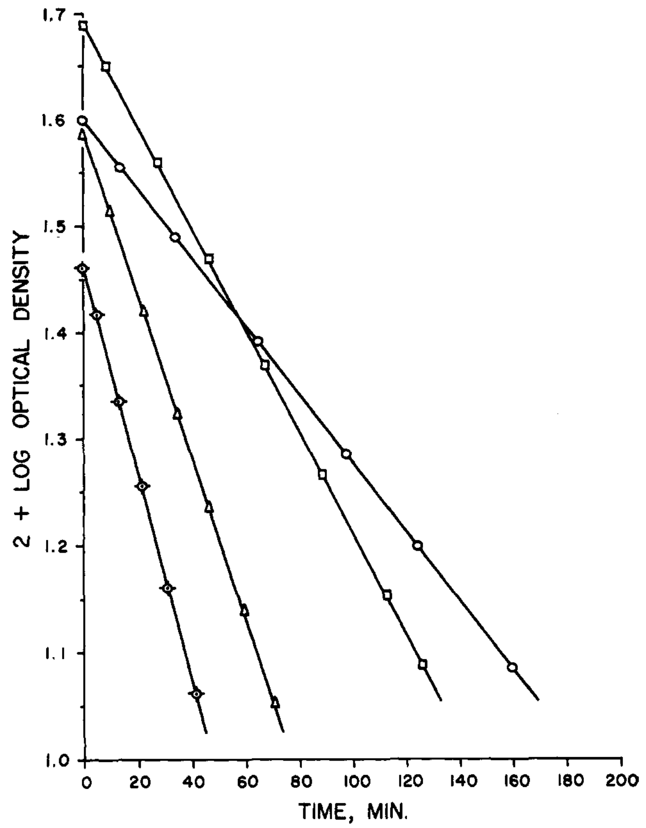

Fig. 2.—The fading reactions in absolute ethanol of irradiated solutions: methyl bis(2,4-dinitrophenyl)acetate, −39.6°, □; ethyl bis(2,4-dinitrophenyl)acetate, −62.3°, ⊕; 2,4,4′-trinitrodiphenylmethane, −76.6°, ○; and 2,4,2′,4′-tetranitrodiphenylmethane, −84.2°, △.

TABLE II

ULTRAVIOLET SPECTRA IN ETHANOL

Compound	λ_{max}, mμ[a]	$\epsilon_{max} \times 10^{-3}$
2,4,4′-Trinitrodiphenylmethane	262	20.0
	248 (sh)	18.2
2,4,2′,4′-Tetranitrodiphenylmethane	242	29.3
	260 (sh)	25.4
Methyl 2,4,4′-trinitrodiphenylacetate	261	22.0
	247 (sh)	20.6
Methyl bis(2,4-dinitrophenyl)acetate	241	31.3
	262 (sh)	24.0
Ethyl 2,4,4′-trinitrodiphenylacetate	261	22.1
	240 (sh)	19.8
Ethyl bis(2,4-dinitrophenyl)acetate	241	31.4
	261.5 (sh)	23.7
p-Nitrotoluene	273[c]	9.5
4,4′-Dinitrodiphenylmethane	277[b]	23.0
2,4′-Dinitrodiphenylmethane	266[b]	15.0
2,4-Dinitrotoluene	240.5[c]	14.3
2,4-Dinitro-1-ethylbenzene	241[c]	12.9
2,4-Dinitrophenylacetic acid	242	

[a] sh is shoulder. [b] Ref. 9. [c] W. A. Schroeder, *et. al.*, *Anal. Chem.*, **23**, 1740 (1951).

the preceding structure may approximate that of the activated complex.

The quinoid ring and ring formed by the hydrogen bond lie in the same plane. The possibility exists that for 2,4,2′,4′-tetranitrodiphenylmethane both *o*-nitro groups could be involved at the same time in the activated complex, with each of the methylene hydrogen atoms. This is probably not the case, however, since the activation energy of IV is about the same as I, II, and III. As in the case of the benzylpyridines the values of E_{exp} fell in the range normally observed for hydrogen bonds.[1,11] Values of the frequency factor were found to be in the range 10^2–10^3 sec.$^{-1}$, similar to the low values observed for benzylpyridines.[1]

Ultraviolet Spectra.—The three trinitro compounds (III, V, VI) each show a broad absorption band with λ_{max} at 261–262 mμ and a distinct shoulder at shorter wave lengths (240–248 mμ). On introduction of the fourth nitro group λ_{max} shifts 20 mμ in each case, to shorter wave lengths and appears at 241–242 mμ. The original 261-mμ band now appears as a slight shoulder at 260 mμ. In addition, there is a considerable enhancement of the absorption intensity. In each case, ϵ_{max} increases by 9300 units. These data, as well as the absorption characteristics of several reference compounds, are listed in Table II.

Two distinct N → V bands are frequently observed in the spectra of *meta*-substituted benzenes,[12] and have recently been reported by Kamlet and co-workers[13] in an analysis of the spectra of alkyltrinitrobenzenes. These investigators attribute the absorption which they designate band A to an electronic transition in the direction (alkyl-$C^+_{para} \rightarrow C{=}NO_2^-$) and band B to a similar transition which is not exactly equivalent, since it involves another nitro group interacting with its *para*-unsubstituted ring carbon atom ($C^+_{para} \rightarrow C{=}NO_2^-$).

In the present study, the absorption band at 261–262 mμ in the spectra of the trinitro compounds and the shoulder at 260–262 mμ in the spectra of the tetranitro compounds can be identified with band A, *i.e.*, a transition in the methylene–nitro axis. This transition would be expected to give rise to the longer wave-length band, since *p*-alkyl-substituted nitrobenzenes show a bathochromic shift in relation to nitrobenzene.[14] This 261–262-mμ absorption band corresponds to the 273-mμ band in *p*-nitrotoluene and the 277-mμ band in 4,4′-dinitrodiphenylmethane. In the trinitro compounds the displacement of band A to 260 mμ can be accounted for in the case of the dinitro-substituted ring, as due to the normal hypsochromic effect of the second nitro group.[13] Absorption due to the same electronic transition in the mononitro-substituted ring might still be expected at approximately 275 mμ. However, it has been reported[9] that 2,4′-dinitrodiphenylmethane absorbs at 266 mμ. The presence of a nitro group in the *ortho* position of the second ring apparently increases the energy required for the electronic transition.

The absorption band at 241–242 mμ observed for the tetranitro compounds and the shoulder at 240–248 mμ observed for the trinitro compounds is assigned as band B. In the former compounds it arises from the two equivalent transitions ($C^+_5 \rightarrow C_2{=}NO_2^-$) and ($C^+_{5'} \rightarrow C_{2'}{=}NO_2^-$). The presence of this band at 241–242 mμ is in keeping with the occurrence of the absorption band in 2,4-dinitrotoluene, 2,4-dinitro-1-ethylbenzene, and 2,4-dinitrophenylacetic acid at these wave lengths. The large increase in over-all absorption

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(11) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 57.

(12) W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958).

(13) M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, *J. Am. Chem. Soc.*, **84**, 3925 (1962).

(14) W. G. Brown and H. Reagan, *ibid.*, **69**, 1032 (1947).

intensity observed in the tetranitro compounds can be attributed to the fact that there are now two rings in which the nitro groups are oriented *meta* with respect to each other.[12,13] This effect has been attributed to reduced force constants of the N-nuclear bonds caused by the electron-withdrawing effect of the nitro substituents.[15]

Experimental[16]

Methyl *p*-nitrophenylacetate was prepared from the corresponding acid and melted at 51–52°, lit.[17] m.p. 54°.

Methyl 2,4-dinitrophenylacetate prepared from the corresponding acid melted at 79–81°, lit.[18] m.p. 82–83°.

1-Bromo-2,4-dinitrobenzene was recrystallized Eastman Organic Chemicals product, m.p. 71–72°.

Ethyl diphenylacetate was prepared by esterification of the corresponding acid and melted at 54–55°, lit.[19] m.p. 57°.

Methyl Bis(2,4-dinitrophenyl)acetate (I).—In a dry 500-ml. round-bottomed flask with a magnetic stirring bar and fitted with a calcium sulfate drying tube, 0.48 g. (0.021 g.-atom) of sodium was added to 13 ml. of commercial anhydrous methanol. After the sodium had dissolved, and with stirring, 5 g. (0.021 mole) of methyl 2,4-dinitrophenylacetate in 50 ml. of dry methanol was added followed after 5 min. with 5.15 g. (0.021 mole) of 2,4-dinitrobromobenzene in 100 ml. of methanol. A deep green color appeared immediately which within minutes became blue. After stirring at room temperature for 4.5 hr. the mixture was acidified with 10% nitric acid. This gave a colorless solution from which the product separated within minutes. Filtration of the chilled mixture yielded sparkling white crystals melting at 161–162°. Recrystallization from 50% methanolic benzene furnished 3.42 g. of I, m.p. 162–163°, lit.[5] m.p. 159°.

Anal. Calcd. for $C_{15}H_{10}N_4O_{10}$: C, 44.34; H, 2.48; N, 13.79. Found: C, 44.63; H, 2.49; N, 13.89.

Ethyl Bis(2,4-dinitrophenyl)acetate (II).—This was prepared according to the procedure of Werner[6] by the nitration of ethyl diphenylacetate, and melted at 155–156°, lit.[6] m.p. 154°.

Ethyl 2,4,4′-trinitrodiphenylacetate (VI).—Into a stirred solution of 1 g. (0.043 g.-atom) of sodium in 50 ml. of absolute ethanol in a dry atmosphere a solution of 7.80 g. (0.040 mole) of methyl *p*-nitrophenylacetate in 300 ml. of ethanol and a solution of 10 g. (0.040 mole) of 2,4-dinitrobromobenzene in 300 ml. of ethanol were added simultaneously. The addition at room temperature was carried out over a 40-min. period, and then the mixture was stirred for 1 hr. Acidification of the mixture with 10% nitric acid furnished a white precipitate which was filtered and washed with cold ethanol. Recrystallization from ethanol gave 8.45 g. of VI, melting at 108–109°. Recrystallization raised the melting point to 110–111°.

Anal. Calcd. for $C_{16}H_{13}N_3O_8$: C, 51.20; H, 3.49; N, 11.20. Found: C, 51.17; H, 3.51; N, 11.41.

Methyl 2,4,4′-trinitrodiphenylacetate (V).—The preceding ester (VI, 3 g.) was combined with 22 ml. of concentrated sulfuric acid in an open erlenmeyer flask, and was heated on a steam bath for 10 min. Water (15 ml.) was added to the heated solution over the next 5 hr. by adding 1 ml. of water every 20 min. At this time there was some insoluble taffylike material present. After heating for an additional hour, the mixture was chilled, the solid was powdered, collected on a filter, and washed with water. Three recrystallizations from benzene furnished 1.57 g. of cream-colored crystals which melted with previous softening and effervescence at 73–75°. This material was stored in the refrigerator. The product, presumably 2,4,4′-trinitrodiphenylacetic acid, showed C=O at 5.93 μ and the broad absorption characteristic of the OH group in acids at 3–4 μ. The precursor showed the ester C=O at 5.85 μ. This acid (1 g. or 0.003 mole) in an erlenmeyer flask was chilled in ice and an ethereal diazomethane solution containing approximately 0.03 mole of diazomethane was added. The reaction was very rapid. The solution was kept cold for 15 min. and then was allowed to stand at room temperature at which time pale yellow crystals deposited. After standing overnight the residual oily crystals were recrystallized from methanol and melted at 95–97° (0.71 g.). Further recrystallization raised the melting point to 96–98°.

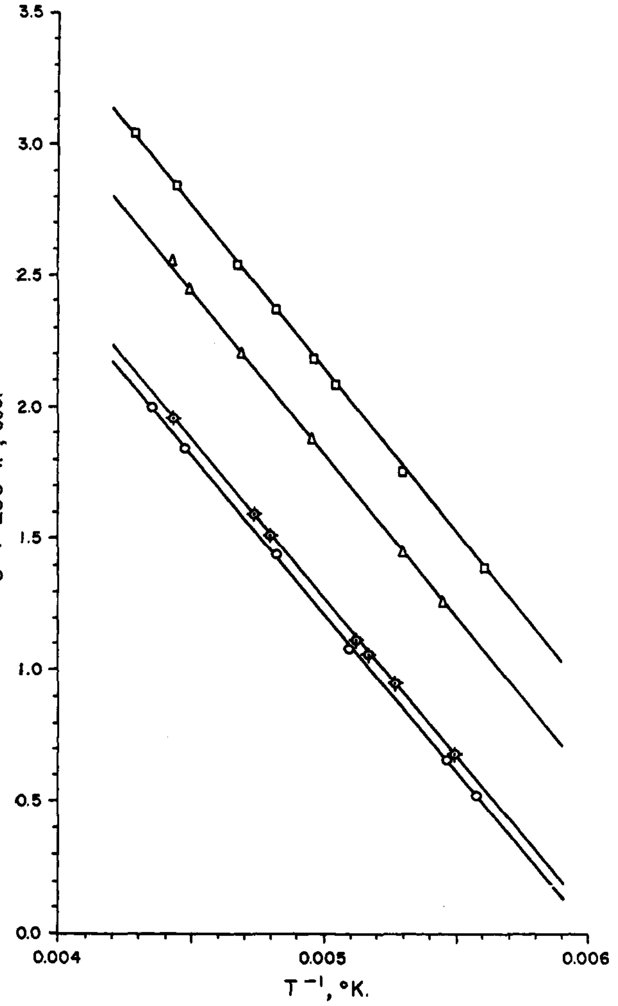

Fig. 3.—Plots of log *k* values *vs.* 1/*T* for methyl bis(2,4-dinitrophenyl)acetate, □; ethyl bis(2,4-dinitrophenyl)acetate, ⊕; 2,4,4′-trinitrodiphenylmethane, O; and 2,4,2′,4′-tetranitrodiphenylmethane, Δ (all in ethanol).

Anal. Calcd. for $C_{15}H_{11}N_3O_8$: C, 49.87; H, 3.07; N, 11.63. Found: C, 49.86; H, 3.05; N, 11.77.

2,4,4′-Trinitrodiphenylmethane (III).—This was obtained by warming 2 g. of 2,4,4′-trinitrodiphenylacetic acid (obtained as in the preceding reaction) in 25 ml. of ethanol containing a small amount of charcoal. Decarboxylation was complete within 5 min., at which time solid began to precipitate. Additional ethanol (50 ml.) was added from which the solid was recrystallized to yield 1.52 g. of cream-colored crystals which melted at 109–110°. Further recrystallization raised the melting point to 110–111°, lit.[9] m.p. 107–110°.

2,4,2′,4′-Tetranitrodiphenylmethane (IV).—Ethyl bis(2,4-dinitrophenyl)acetate was hydrolyzed to the acid by the procedure used in the preparation of V. The unpurified acid melted after one recrystallization from benzene at 200–208° with effervescence. The acid was decarboxylated in warm ethanol as in the preceding reaction. The product (IV), recrystallized from benzene, melted at 175–176°, lit.[8] m.p. 173°.

Kinetic Measurements.—Samples used for rate studies were purified by several crystallizations. The final melting points were constant. Spectro Grade ethanol was dried by conventional methods. The solutions for measurement were approximately 10^{-3} *M*.

The rate studies at low temperatures in the range −95.0 to −39.6° were carried out in a 2.5-cm. cell maintained at the required temperature in a specially constructed cryostat[20] which

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[15] W. F. Forbes and J. F. Templeton, *Can. J. Chem.*, **36**, 180 (1958).

[16] Melting points were taken on a Fisher-Johns block and are uncorrected.

[17] T. Maxwell, *Ber.*, **12**, 1764 (1879).

[18] V. Meyer and A. Meyer, *ibid.*, **21**, 1304 (1888).

[19] H. Staudinger and J. Siegwart, *ibid.*, **49**, 1918 (1916).

[20] J. A. Sousa and J. Weinstein, *Rev. Sci. Instr.*, **34**, 150 (1963).

could regulate temperatures within ±0.1° for at least 6 hr. Solutions cooled in the cryostat were exposed for 15–60 sec. to the unfiltered radiation from a Hanovia-type 16,200 lamp with a quartz envelope. Uniform coloring of the solutio was observed. The cryostat was quickly transferred to the sample cell compartment of a Cary Model 14 spectrophotometer and the decrease in absorbance of the visible band at λ_{max} was followed with respect to time. A matched cell containing pure ethanol was in the reference beam. In all cases the absorbance of the system ultimately fell to zero. At least two runs were made at each temperature.

Values of the first-order specific rate constant, k, were calculated from the slope of the straight line in plots of log optical density *vs.* time. The reaction was followed for at least two half-lives. Illustrative plots are given in Fig. 1. The Arrhenius activation energy, E_{exp}, was calculated from the slope of the straight line obtained in plots of log k *vs.* $1/T$. The entropy of activation, ΔS^*, was calculated using the following equation.[21]

$$k = e\frac{\bar{k}T}{h}e^{\Delta S^*/R}\,e^{-E_{exp}/RT}$$

The frequency factor, A, in the Arrhenius equation, $k = Ae^{-E_{exp}/RT}$ was calculated from the following relationship.

$$A = e\frac{\bar{k}T}{h}e^{\Delta S^*/R}$$

Ultraviolet and Visible Absorption Measurements.—A Cary Model 14 spectrophotometer was used The compounds were dissolved and measured in absolute Spectro Grade ethanol. The ultraviolet absorption spectra were measured in a 1-cm. cell against a reference of pure solvent in a matched cell. The visible irradiation spectra of Fig. 2 were obtained by exposing cryostated solutions at −103.5° for 2 min. to the unfiltered radiation from a Hanovia lamp and measuring against a reference of pure solvent. The anionic spectra of Fig. 2 were obtained at room temperature by adding to the ethanol solutions one drop of 0.01 N potassium hydroxide.

Acknowledgment.—The authors wish to thank Mr. C. DiPietro for the chemical analyses.

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(21) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

The Nuclear Magnetic Resonance Spectra of Heterocyclic Compounds. III. Synthesis and Spectra of Steroids Having 20,21-Bisethylene Dioxide Moieties[1]

E. CASPI,[2a] H. ZAJAC,[2b] AND TH. A. WITTSTRUCK

Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts

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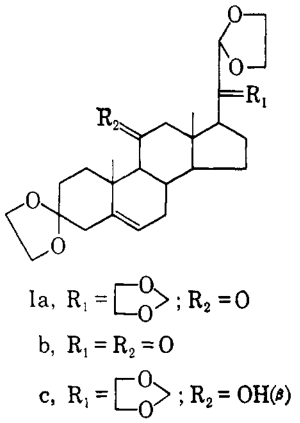
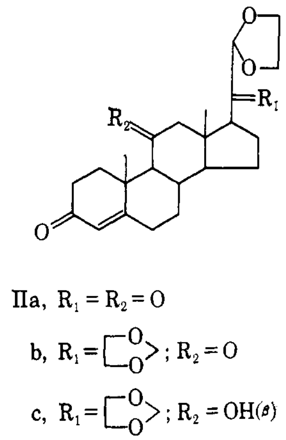
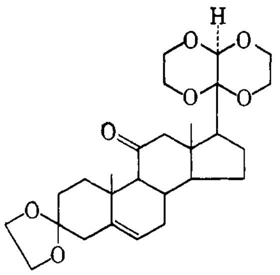
The product of ethylene glycol-*p*-toluenesulfonic acid treatment of the 3,21-bisethylene dioxide (Ib) was found to be identical with the by-product of cortisone ketalization.[3] The previously proposed n.m.r. generalizations for steroidal dioxolanes were confirmed. Compounds with 20,21-bisethylene dioxide (Ia) and 17β-naphthodioxane (III) moieties were isolated as important ketalization by-products of cortisone.[3] Assignment of structures I and II was based largely on n.m.r. evidence. An extension of this work is described in the present article.

In the first paper of this series, studies of the n.m.r. spectra of simple substituted dioxolanes, dioxanes, and naphthodioxanes were presented.[4] It was shown that the single proton on a carbon bearing two oxygens in a five-membered ring gives a resonance at about 5.0–5.2 τ, while a single proton at the bridgehead of *trans*-1,4;5,8-naphthodioxane gives a resonance[5] at 5.35 τ. Furthermore, the signal for the $-O-CH_2-CH_2-O-$ moiety of the dioxolane derivatives in general did not exhibit resolvable splitting from the coupling between the methylene protons, and hence appeared as a relatively narrow signal. In contrast, the corresponding resonance for naphthodioxane was resolvable into a broad multiplet. These observations and reference values were important features in assigning structures I and III. However, since the reference values were obtained for simple dioxolanes and *trans*-1,4;5,8-naphthodioxane, it appeared desirable to verify these for steroids and also to confirm structures Ia and Ic.

Our first objective was to prepare a steroidal *aldehydo*-ethylene dioxide and to evaluate the chemical shift for the single proton on the carbon bearing two oxygens. Several routes to such compounds were considered, and the most appropriate appeared to be that described by Tsuda, *et al.*[6] Indeed, when cortisone was







III

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(1) This work was supported by Grants CY-4663 and A-5326 from the U. S. Public Health Service.

(2) (a) Recipient of a Public Health Service research career program award CA-K3-16614 from National Cancer Institute; (b) Post Doctoral Fellow (1962-1963) on leave of absence from the Technical University, Lodz, Poland.

(3) E. Caspi, Th. A. Wittstruck, and N. Grover, *J. Org. Chem.*, **28**, 763 (1963).

(4) E. Caspi, Th. A. Wittstruck, and D. M. Piatak, *ibid.*, **27**, 3183 (1962).

(5) Page 3189, line 22 in ref. 3 should read *trans*-1,4;5,8-naphthodioxane.

(6) K. Tsuda, N. Ikekawa, and S. Nozoe, *Chem. Pharm. Bull.* (Tokyo), **7**, 519 (1959).