TABLE II

NITRITE PHOTOLYSIS PRODUCT COMPOSITION

	Starting nitrite							
Product	Ethyl	Propyl	2-Methyl-1-propyl	2,2-Dimethyl-1-propyl	2-Propyl	2-Butyl	3-Methyl-2-butyl	3,3-Dimethyl-2-butyl
Nitrosomethane dimer	0%	..	..	....	0%	..	..	....
Nitrosoethane dimer	..	0%	..	....	..	7%	..	....
2-Nitrosopropane dimer	..	..	0%[a]	....	..	..	31%	....
2-Nitroso-2-methylpropane	..	..	..	7.5%	..	..	..	8.5%[b]
Methanal	0%	0%	18%	35%	..	..	..	....
Ethanal	40%	..	..	....	0%	10%	46%	64%
Propanal	..	40%	..	....	..	..	..	....
2-Methyl-1-propanal	..	..	12%	....	..	..	..	....
2,2-Dimethyl-1-propanal	..	..	..	5.7%	..	..	..	....
2-Propanone	..	..	..	....	30%	..	..	....
2-Butanone	..	..	..	....	..	29%	..	....
3-Methyl-2-butanone	..	..	..	....	..	..	2%	....
3,3-Dimethyl-2-butanone	..	..	..	..	..	..	..	7.4%
Ethanol	34%	..	..	....	..	..	..	....
Propanol	..	29%	..	....	..	..	..	....
2-Methyl-1-propanol	..	..	27%	....	..	..	..	....
2,2-Dimethyl-1-propanol	..	..	..	8.1%	..	..	..	....
2-Propanol	..	..	..	....	23%	..	..	....
2-Butanol	..	..	..	....	..	31%	..	....
3-Methyl-2-butanol	..	..	..	....	..	..	18%	....
3,3-Dimethyl-2-butanol	..	..	..	....	..	..	..	16%

[a] No isomeric oxime found. [b] 40% yield of isobutene found.

Levy and Copeland[6] reported that reaction 2 is accompanied by reaction 3 and that the thermal

$$2HNO \longrightarrow N_2O + H_2O \qquad (3)$$

decomposition of 2,2'-azoisobutane in the presence of nitric oxide yielded 2-nitroso-2-methylpropane, isobutene and nitrous oxide. Again there was no evidence for the formation of hydroxamic acid, reaction 4.

$$(CH_3)_3CNO + CH_3CHO \not\longrightarrow (CH_3)_3CN(OH)COCH_3 \qquad (4)$$

Secondary alkoxy radicals undergo the radical decomposition reaction with greater ease than do the corresponding primary alkoxy radicals, as evidenced by the greater yield of aldehyde cleavage product. The yield of ethanal increased as the alkyl radical from the radical decomposition reaction of secondary alkoxy radicals varied from ethyl to isopropyl and *t*-butyl. This order is identical with the well known order of stability of simple alkyl radicals, *i.e.*, tertiary > secondary > primary.

Experimental

Material, apparatus, photolysis procedure and analytical methods were as described in Parts I, II and III.

Acknowledgment.—The authors wish to acknowledge the technical assistance of members of this Laboratory and in particular Mr. R. Armswood. The authors are indebted to Prof. D. H. R. Barton and Dr. E. B. Hershberg for their helpful interest in this work.

---

(6) J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DIVISION, SCHERING CORPORATION, BLOOMFIELD, N. J.

Photolysis of Nitrite Esters in Solution. V. Photochemistry of Cyclohexyl Nitrites

BY PETER KABASAKALIAN AND EDWARD R. TOWNLEY

RECEIVED MARCH 4, 1961

Photolysis of alkyl cyclohexyl nitrites in benzene indicated that only the conformationally favored disubstituted cyclohexane derivatives, the ones vicinally substituted, capable of forming six-membered ring intermediates gave 30–40% yields of nitroso dimers. Cyclohexyl alkyl nitrite photolyses gave further evidence in the support of the basic prerequisite of a six-membered ring intermediate in the Barton reaction.

Introduction

Four previous publications[1] in this series have established that the photolysis of primary, secondary and tertiary alkyl nitrites produces simple nitroso compounds by the *alkoxy radical decomposition mechanism* and hydroxy nitroso compounds by the *alkoxy radical rearrangement mechanism* (the Bar-

---

(1) (a) P. Kabasakalian and E. R. Townley, *J. Am. Chem. Soc.*, **84**, 2711 (1962), part I; (b) P. Kabasakalian, E. R. Townley and M. D. Yudis, *ibid.*, **84**, 2716 (1962), part II; (c) *ibid.*, **84**, 2718 (1962), part III; (d) P. Kabasakalian and E. R. Townley, *ibid.*, **84**, 2723 (1962), part IV.

ton reaction[2]). In the present study, further evidence was sought for establishing the conformational requirements of the six-membered ring intermediate in the Barton reaction using cyclohexyl derivatives.

Results

The yields of nitroso dimers (as indicated by their molar absorptivity values at about 294 $m\mu$) resulting from the photolysis of alkyl substituted cyclohexyl nitrites in benzene are shown in Table I.

TABLE I

EFFECT OF SUBSTITUTION ON NITROSO DIMER YIELD FROM CYCLOHEXYL NITRITES

Isomer, % *cis*	Isomer, % *trans*	Starting nitrite	Product[a] ϵ
		Cyclohexyl	200
45	55	2-Methyl-1-cyclohexyl	400
63	37	3-Methyl-1-cyclohexyl	100
39	61	4-Methyl-1-cyclohexyl	100
48	52	4-Cyclohexyl-1-cyclohexyl	100
29	71	2-Ethyl-1-cyclohexyl	3000
48	52	2-Cyclohexyl-1-cyclohexyl	3600

[a] For 100% yield $\epsilon \sim 9{,}500$ ($\lambda_{max} \sim 294\ m\mu$).

The effect of alkyl chain length in the yield of nitroso dimer from the photolysis of cyclohexyl substituted alkyl nitrites is illustrated in Table II. The photolysis of 3-cyclohexyl-1-propyl nitrite yielded 3-(1-nitroso-1-cyclohexyl)-1-propanol monomer which was qualitatively identified by its visible absorption maximum at 680 $m\mu$[3] and infrared absorption maximum at 6.4 μ,[4] characteristic of tertiary nitroso monomers. Quantitative estimation of the yield of nitroso monomer was made by polarographic analysis.[1c] The yield reported for 3-(1-nitroso-1-cyclohexyl)-1-propanol monomer is the peak value obtained when only a fraction of the nitrite had been converted to photolytic products. The concentration of this tertiary nitroso monomer reached a limiting value early in the photolysis and remained there throughout the reaction. All other product yields are for complete photolysis runs.

TABLE II

EFFECT OF ALKYL CHAIN LENGTH ON NITROSO DIMER YIELD

Starting nitrite	Product[a] ϵ
1-Cyclohexyl-1-methyl	400
2-Cyclohexyl-1-ethyl	2800
3-Cyclohexyl-1-propyl	0[b]
4-Cyclohexyl-1-butyl	4000

[a] For 100% yield $\epsilon \sim 9{,}500$ (λ_{max}, $\sim 294\ m\mu$). [b] 31% yield of 3-(1-nitroso-1-cyclohexyl)-1-propanol obtained.

Discussion

The results of the photolysis of *cis* and *trans* mixtures of alkyl substituted cyclohexyl nitrites (Table I) are in agreement with previous findings[1] requiring a six-membered ring intermediate in the Barton reaction. Nitroso dimers, nitroso monomers or oximes were formed in only small amounts when cyclohexyl, 2-methyl-1-cyclohexyl, 3-methyl-1-cyclohexyl, 4-methyl-1-cyclohexyl and 4-cyclohexyl-1-cyclohexyl nitrites were photolyzed. These results are entirely rational when one considers that the formation of the prerequisite six-membered ring intermediate is much unfavored on steric grounds. Thus cyclohexyl nitrite would have to react in the unstable boat form to yield a six-membered ring intermediate which eventually would give 4-nitrosocyclohexanol dimer. The same is true for the *cis* isomers of 4-methyl- and 4-cyclohexyl-1-cyclohexyl nitrites[5] (Table III). The *trans* isomers of 1,4- and 1,3-disubstituted cyclohexanes cannot form six-membered ring intermediates. *cis*-3-Methyl-1-cyclohexyl nitrite would require the unstable *diaxial* conformation to yield the six-membered ring intermediate. *cis*- and *trans*-2-methyl-1-cyclohexyl nitrites can only give the corresponding stable *cis* and *trans* five-membered ring intermediates. However, in the case of 2-ethyl-1-cyclohexyl (I) and 2-cyclohexyl-1-cyclohexyl (II) nitrites, normal yields of nitroso dimers were obtained. The *cis* and *trans* isomers of both substances can form stable six-membered ring intermediates similar to the *cis*- and *trans*-decalins.

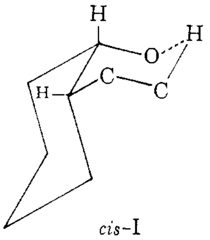
TABLE III

DISUBSTITUTED CYCLOHEXANES

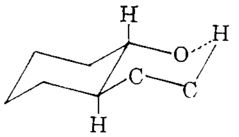
Preferred conformations[a]			Conformational requirements for Barton reaction[c]		
Substn.	*cis* Isomer[b]	*trans* Isomer[b]	Substn.	*cis* Isomer	*trans* Isomer
1,2	*ae*	*ee*	1,2	*ae*	*ee*
1,3	*ee*	*ae*	1,3	*aa*	Not poss.
1,4	*ae*	*ee*	1,4	*aa*[d]	Not poss.

[a] Chair conformation. [b] *a*, axial bond; *e*, equatorial bond. [c] Basic prerequisite of a six-membered ring intermediate. [d] Boat conformation.

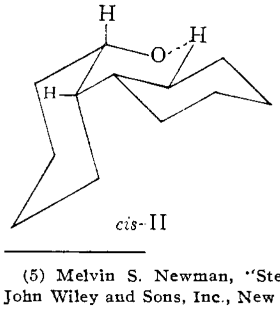
It should be noted that the yield (*ca.* 30%) of nitroso dimer from I involving intramolecular transfer of a primary hydrogen atom is very much higher than those reported (*ca.* 5%) in part III for the completely flexible straight chain molecules while the yield (*ca.* 40%) of nitroso dimer from II involving intramolecular secondary hydrogen transfer is similar to those reported (30–40%) in part III. The higher yield in the case of 2-ethyl-1-cyclohexyl nitrite undoubtedly is due to the favored conformation already present in the mole-



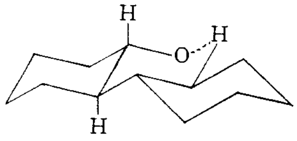
cis-I



trans-I



cis-II



trans II

---

[2] D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *ibid.*, **82**, 2640 (1960).

[3] J. R. Schwartz, *ibid.*, **79**, 4353 (1957).

[4] B. G. Gowenlock and W. Luttke, *Quart. Revs.*, **12**, 321 (1958).

[5] Melvin S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

cule. Evidently the geometric factor dominates the structural factor when primary hydrogen atoms are involved in the Barton reaction, while the inverse is true when secondary hydrogen atoms are involved.

The photolysis of cyclohexylmethyl nitrite gave a very small yield (4%) of nitroso dimer while 2-cyclohexyl-1-ethyl nitrite gave a fair yield (30%) of nitroso dimer (Table II). These results are consistent with the behavior of alkyl substituted cyclohexyl nitrites in that good yields of nitroso dimers were obtained only when a stable six-membered ring intermediate could be formed, as with the latter substance.

Further evidence in support of the basic prerequisite of a six-membered ring intermediate in the Barton reaction was obtained during the photolysis of three nitrites which had tertiary hydrogen atoms in appropriate positions, 2-cyclohexyl-1-ethyl, 3-cyclohexyl-1-propyl and 4-cyclohexyl-1-butyl nitrites. In the three compounds cited above, a tertiary hydrogen atom was available for intramolecular hydrogen abstraction which would involve five-, six- and seven-membered ring intermediates, respectively. Evidence of the attack on the tertiary hydrogen atom would be obtained easily from the fact that the resulting tertiary nitroso monomer which would not dimerize in solution, would show a weak visible absorption band at 680 mμ ($\epsilon \sim 20$).

No evidence for the formation of any tertiary nitroso monomer was found during the photolyses of 2-cyclohexyl-1-ethyl and 4-cyclohexyl-1-butyl nitrites. Only in the photolysis of 3-cyclohexyl-1-propyl nitrite where the tertiary hydrogen atom available for hydrogen abstraction can take part in a six-membered ring intermediate was there any evidence for the production of tertiary nitroso monomer (31%). The nitroso dimer yield fell to zero.

Experimental

Material, apparatus, photolysis procedure and analytical methods were as described in Parts I, II and III. The *cis* and *trans* isomer contents of the cyclohexyl alcohols were determined by vapor phase chromatography following the procedure of Komers, Kochloefl and Bazant.[6]

Acknowledgments.—The authors wish to acknowledge the technical assistance of members of this Laboratory and in particular Mr. R. Armswood. The authors are indebted to Prof. D. H. R. Barton and Dr. E. B. Hershberg for their helpful interest in this work.

---

[6] R. Komers, K. Kochloefl and V. Bazant, *Chemistry & Industry*, 1405 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

The Structure and Chemistry of Ferrocene. VI. Mechanism of the Arylation Reaction[1]

BY M. ROSENBLUM, W. GLENN HOWELLS,[2] A. K. BANERJEE AND C. BENNETT[3]

RECEIVED MARCH 5, 1962

The reaction of ferrocene with aryldiazonium salts prepared from aniline, *p*-aminoacetophenone and *p*-anisidine yields not only mono- and 1,1′-diarylferrocenes, but 1,2- and 1,3-diarylferrocenes as well. Structural assignments for these latter two types of derivatives have been made on the basis of unambiguous synthesis and infrared spectral correlations. The view that arylferrocenes are formed in these reactions by attack of free aryl radicals on either ferrocene or on the ferricinium cation is shown to be without experimental support. A new mechanism involving internal rearrangement of a ferrocene–diazonium salt charge-transfer complex is proposed. The broader theoretical implications of these conclusions are discussed.

Introduction

The very great reactivity of ferrocene toward electrophilic reagents prompted an early examination of its reaction with aryldiazonium salts with the expectation of securing azoferrocenes.[4] Although these designs were frustrated, the outcome proved nevertheless to be of considerable interest since the products were the otherwise difficultly accessible arylferrocenes. At present this reaction constitutes the simplest and most direct method for the preparation of these substances.

Our interest in these reactions was initially confined to the preparation of a variety of arylferrocenes to be used in connection with other studies. However, certain observations led us to examine the reaction in greater detail. The present report is an account of these studies and of our conclusions regarding the mechanism of these transformations and their broader implications.

Results

The arylation of ferrocene has been reported to afford monoarylferrocenes together with 1,1′-diarylferrocenes. Broadhead and Pauson[4c] alone have described the isolation of a substance isomeric with 1,1′-bis-*p*-methoxyphenylferrocene, obtained in the treatment of ferrocene with diazotized *p*-anisidine. They were unable to determine whether this substance was an authentic diarylferrocene (structure II or III) or a biphenylyl derivative similar in constitution to *p*-biphenylylferrocene isolated from the reaction of ferrocene with phenyl diazonium chloride.[5] Mostly on the basis of their

---

[1] This research was supported by a grant (RG-5978) from the National Institutes of Health, Public Health Service, and by the Office of Ordnance Research, U. S. Army, under contract (DA-19-020-ORD-4757).

[2] Taken in part from a dissertation submitted by W.G.H. in partial fulfillment of the requirements for the Ph.D. degree, June, 1961.

[3] National Science Foundation Undergraduate Research Participant, under grant 15867, Summer, 1961.

[4] (a) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954); (b) A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *ibid.*, **99**, 539 (1954); (c) C. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[5] P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).