Calcd. for $C_6H_{12}O_3N_2$: C, 44.99; H, 7.55; N, 17.49. Found: C, 45.07; H, 7.71; N, 17.53.

The elimination of nitrous oxide was carried out using the procedure given above for the nitrosoamides.

The Reaction of Isobutylamine with Nitrous Acid.—Isobutylamine (14.9 g., 0.204 mole) was added to 300 ml. of 0.8 *N* sulfuric acid (0.24 mole) at 0° and a solution of sodium nitrite (25 g., 0.36 mole) in 50 ml. of water was slowly added. After one day, 25 ml. of 1.0 *N* sulfuric acid was added, and after an additional day at 0°, the solution was saturated with sodium chloride and the alcohols extracted with ether (the aqueous solution yielded 1.9 g. of unreacted amine, 0.026 mole, 13%). The ether solution was washed with dilute sodium hydroxide solution (5%), the solution was dried, and the ether removed through a small column. The mixture of alcohols was distilled at 1 atm., the fraction boiling from 65 to 120° weighed 2.9 g. (0.04 mole, 22% based on the amine which had reacted). The infrared spectrum indicated that the alcohols were contaminated with small amounts of nitroalkanes and nitrates. The isomer distribution given in Table I was determined by comparing the infrared spectrum of the product with the spectra of mixtures of the authentic alcohols. This isomer distribution was confirmed by the infrared spectrum of the 3,5-dinitrobenzoates prepared by treating the alcohol mixture with 3,5-dinitrobenzoyl chloride in an excess of pyridine. The analyses given are good to within *ca.* 5%.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION NO. 1264 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

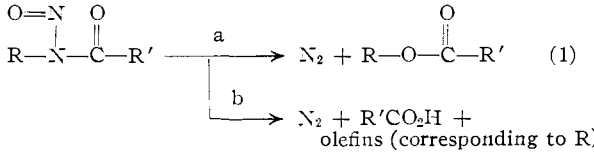
The Chemistry of the N-Alkyl-N-nitrosoamides. III. Mechanism of the Nitrogen Elimination Reaction[1]

BY EMIL H. WHITE

RECEIVED DECEMBER 23, 1954

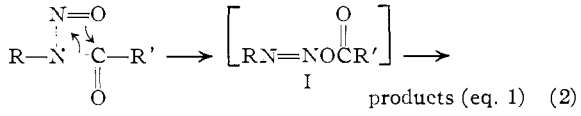
A two-stage mechanism is proposed for the rearrangement of a N-alkyl-N-nitrosoamide into the corresponding ester. The formation of a diazo ester represents the first stage, and the elimination of nitrogen from the diazo ester *via* a Si reaction, the second. Studies with optically active nitrosoamides have shown that, depending on the reaction conditions, the products from the second stage may be formed by intramolecular retention, intramolecular inversion or intermolecular inversion reactions.

In the preceding paper[2] it was shown that, stoichiometrically, the elimination of nitrogen from the N-alkyl-N-nitrosoamides occurs according to equation 1.



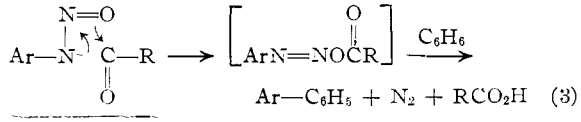
(1)

A single-stage mechanism does not seem possible for this intramolecular reaction; the following mechanism, based upon reactions of the analogous N-nitroamides and the N-aryl-N-nitrosoamides, satisfactorily accounts for the main features of the reaction.



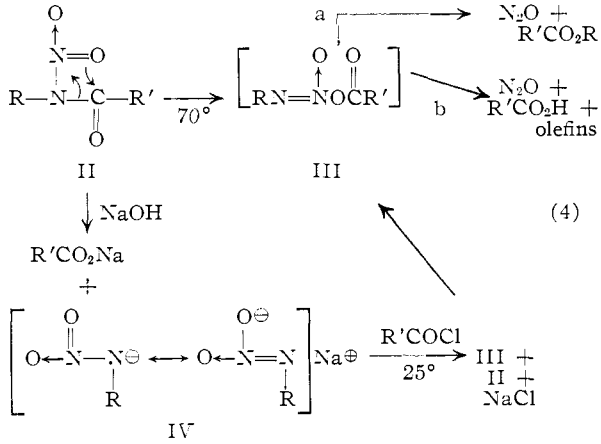
(2)

Formation of the Diazo Ester (I).—In the aromatic series, the formation of a diazo ester from the corresponding nitrosoamide has long been assumed to be the first step in the modified biaryl synthesis.[3] Recent kinetic studies by Huisgen[4] and Hey[5] have confirmed this view. Aliphatic diazonium salts and diazo esters have never been isolated; however, indirect evidence for the intermediate formation of a diazo ester in the reactions of aliphatic nitrosoamides was obtained from a study of the corresponding N-nitroamides.



(3)

N-Nitroamides and N-nitrosoamides under the same reaction conditions eliminate nitrous oxide and nitrogen, respectively, to form olefins and esters in approximately the same yields.[2] The mechanisms for the two reactions are probably very similar; that proposed for the N-nitroamides is given in the upper line of equation 4.



(4)

The unstable intermediate in this case (III) can be obtained by an independent route. The N-nitroamide was saponified to yield the sodium salt of a N-nitroamine IV. Acylation of this salt can occur either on nitrogen or on oxygen, *i.e.*, to yield II or III. N-Nitroamides II are stable under the reaction conditions employed in the last step, whereas the intermediate III should eliminate nitrous oxide

(1) Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 30, 1955.

(2) E. H. White, THIS JOURNAL, **77**, 6011 (1955).

(3) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 228.

(4) R. Huisgen, *Ann.*, **574**, 184 (1951), and four earlier papers.

(5) D. H. Hey, J. Stuart-Webb and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).

according to equations 4a,b.[6] Experimentally, II and the products of equations 4a,b were obtained from the sodium salt–acid chloride reaction (where R = isobutyl and R′ = 3,5-dinitrophenyl); this indicates that "diazoxy esters" (III) are intermediates in the thermal elimination of nitrous oxide from N-nitroamides, and that diazo esters I, by analogy, are intermediates in the thermal elimination of nitrogen from N-nitrosoamides.[7]

Nitrogen Elimination from the Diazo Ester.—The present discussion is concerned with the reaction leading to the ester (equation 1, path a); that leading to the olefin (path b) will be deferred to the end of the paper.

Although N-aryl and N-alkyl-N-nitrosoamides both rearrange into diazo esters, subsequent reactions of these intermediates differ markedly. The alkyl diazo esters rearrange according to equation 1 in all of the solvents used, including hexane, toluene and acetic acid; whereas the aryl diazo esters in aromatic solvents yield biaryls[8] and in non-aromatic solvents yield complex mixtures of compounds containing none of the corresponding ester (eq. 1, path *a*).[8]

Since aryl diazo esters react typically by homolytic cleavage,[9] it was important to determine whether free radical intermediates are involved in the nitrogen elimination from alkyl diazo esters. The following three facts will illustrate the unimportance of this mode of decomposition in the present case: (i) The elimination of nitrogen from N-(*sec*-butyl)-N-nitrosobenzamide in styrene yielded the ester, acid, olefin and nitrogen (eq. 1) but no polymers[10] or products containing the styrene moiety. (ii) The elimination of nitrogen from N-(isobutyl)-N-nitroso-3,5-dinitrobenzamide in carbon tetrachloride through which a rapid stream of nitric oxide was passed, yielded only products corresponding to eq. 1. Oximes and subsequent reaction products would have been expected if free radical intermediates had been involved.[11] (iii) The nitrogen elimination from N-alkyl-N-nitrosoacetamides and benzamides yielded no carbon dioxide (expected if acyloxy radicals were involved).[12]

(6) The reaction of benzoyl chloride with the silver salt of N-nitropropylamine has been reported to yield propylene and propylbenzoate; the N-nitroamide corresponding to II was not detected (M. J. C. A. Simon Thomas, *Rec. trav. chim.*, **9**, 85 (1890)).

(7) Since nitrous oxide was obtained from the reaction of an acid chloride with IV at −20°, and since II is stable to *ca.* 60°, the rate-determining step in the thermal elimination of nitrous oxide from II, is the formation of III. Similarly, the formation of the diazo ester is the rate-determining step in the nitrogen elimination from the aryl nitrosoamides (see footnote 4) and from the N-alkyl-N-nitrosoamides (see footnote 36). Experimentally, the nitrogen elimination from the N-nitrosoamides in heptane followed first-order kinetics. The relative rates of nitrogen elimination were: R = *t*-butyl > *sec*-butyl > cyclohexyl = α-phenylethyl > isobutyl > *n*-butyl; R′ = 3,5-dinitrophenyl > phenyl > methyl. The former results (which will be published in detail later) as well as the predominant retention of acyl group in acetic acid (Table I, run 14), indicate that the rearrangement into the diazo ester (equation 2) is intramolecular in nature.

(8) As shown by the infrared spectrum of the total product. See also W. A. Waters, *J. Chem. Soc.*, **139**, 113 (1937).

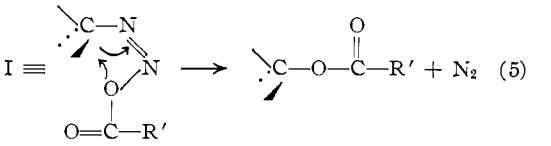
(9) D. H. Hey, *Ann. Repts.*, **37**, 278 (1940); see also footnote 10.

(10) D. H. Hey and G. S. Misra (*Disc. Faraday Soc.*, **2**, 279 (1947)), have shown that radicals from aryl nitrosoamides initiate the polymerization of styrene.

(11) B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).

(12) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949); F. R. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

Other significant features of the nitrogen elimination reaction pertinent to the mechanism are the high yields of relatively isomer free products obtained[2] (compared to the nitrous acid deamination) and the intramolecular nature of the reaction as shown by the formation, predominantly, of *sec*-butyl benzoate from the nitrogen elimination of (+)N-(*sec*-butyl)-N-nitrosobenzamide in acetic acid (Table I, run 14). The *sec*-butyl benzoate from this experiment was obtained with retention of configuration; since a neighboring group effect[13] is not possible in this case, the nitrogen elimination step represents a new type of SNi reaction.[14] By analogy with the mechanisms of other SNi reactions,[14] the following cyclic transition state can be written for this reaction.



It will be shown in the following discussion, however, that this representation alone cannot account for all of the stereochemical results obtained. In order to determine more fully the nature of this reaction, the rearrangement of several optically active nitrosoamides was examined.

Procedure

sec-Butylamine was resolved by the method of Thomé[42] and α-phenylethylamine by the method of Theilacker.[15] In general, optically pure amines were not used, rather, amines of *ca.* 60% optical purity. Amides and nitrosoamides were prepared from these amines by the procedures described in Part I of this series. Since the nitrosamides used were unstable at room temperature, their specific rotations were not determined. The data of Table I are based, therefore, on the optical activities of the starting amides and the esters obtained from them. The observed configurational changes must have occurred during the conversion of the nitrosoamide into the corresponding ester, however, since it had been shown previously that the N-nitrosoamides were formed with no detectable racemization.[40] More specifically, since the rearrangement of the nitrosoamide into the diazo ester does not involve the asymmetric carbon atom (eq. 2), the configurational changes occurred during the elimination of nitrogen from the diazo ester. The configurational changes were calculated using the values for the pure compounds and the relationships listed in Chart I. According to these relationships, *e.g.*, the conversion of (+)N-(*sec*-butyl)-benzamide into (+)*sec*-butyl benzoate represents an over-all retention of configuration.

Results[16]

The wide variety of results obtained (Table I),

(13) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942).

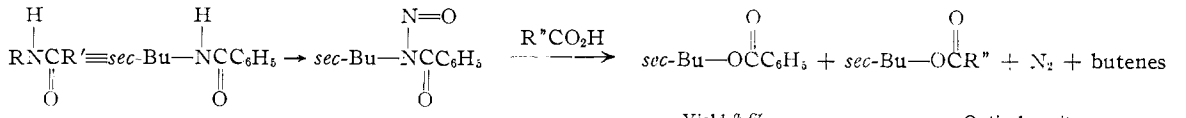
(14) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1267 (1937).

(15) See Chart I, note *h*.

(16) For convenience, the following discussion will be concerned only with the elimination of nitrogen from the intermediate diazo ester, since it is in this step that the configurational changes occur. Unless otherwise noted, R = *sec*-butyl, R′ = phenyl, and R″CO_2H = the added acid.

TABLE I

A. REARRANGEMENT OF OPTICALLY ACTIVE N-(*sec*-BUTYL)-N-NITROSOBENZAMIDE



Run	Solvent	Concn., *M*	Temp., °C.	Added acid or Na_2CO_3	Yield,[a] % Bu–OCC$_6$H$_5$	Yield,[a] % Bu–OCR"	%	Optical purity Bu–OCC$_6$H$_5$[b]	%	Bu–OCR"[c]
1	Pentane	7.6×10^{-2}	25	Benzoic (0.1 *M*)	25		16	Invn.		
2	Pentane	2.5×10^{-2}	25	None	22		11	Invn.		
3	Pentane	4.4×10^{-2}	25	None	26		10	Invn.		
4	Pentane	1.9×10^{-1}	25	Na_2CO_3	25		8	Invn.		
5	Pentane	4.2×10^{-2}	25	Na_2CO_3	22		2	Invn.		
6	Pentane	1.8×10^{-1}	25	Acetic (0.4 *M*)	14	6	5	Retn.	35	Invn.
7	Hexane	3.5×10^{-2}	69	Na_2CO_3	18		7	Retn.		
8	Heptane	3.4×10^{-2}	99	Na_2CO_3	20		8	Retn.		
9	Pentane	2.1×10^{-4}	25	None	18		9	Retn.		
10	Pentane	4.7×10^{-4}	25	Na_2CO_3[d]	12		13	Retn.		
11	Toluene	2.7×10^{-1}	25	3,5-Dinitrobenzoic (0.05 *M*)	14	4	33	Retn.	2	Invn.
12	Homogeneous	.....	10	None	13		34, 35	Retn.		
13	Dimethyl sulfide	2.7×10^{-1}	25	3,5-Dinitrobenzoic (0.1 *M*)	12	3	35	Retn.	6	Retn
14	Acetic acid	4.8×10^{-1}	35	Acetic	12	5	37	Retn.	15	Invn.
15	Pyridine	2.7×10^{-1}	25	3,5-Dinitrobenzoic (0.6 *M*)	9	1	38	Retn.	15	Invn.
16	Dioxane[e]	7.2×10^{-3}	25	None	12		39	Retn.		
17	Dioxane	3.2×10^{-1}	25	None	16		41	Retn.		
18	Dioxane	2.7×10^{-1}	25	3,5-Dinitrobenzoic (0.6 *M*)	12	6	42	Retn.	39	Retn.

B. REARRANGEMENT OF RELATED COMPOUNDS

Run	Reactant	Solvent	Concn., *M*	Temp., °C.	Ester yields,[a] %	Retention,[b] obsd., %
19	N-(*s*-Butyl)-N-nitro-3,5-dinitrobenzamide	Toluene	2.7×10^{-1}	55	25	19
20	N-(*s*-Butyl)-N-nitro-3,5-dinitrobenzamide	Dioxane	2.7×10^{-1}	70	15	31
21	N-(α-Phenylethyl)-N-nitrosoacetamide	Pentane	3.3×10^{-2}	36	35	44
22	N-(α-Phenylethyl)-N-nitrosoacetamide	CCl_4	2.2×10^{-1}	50	..	46
23	N-(α-Phenylethyl)-N-nitrosoacetamide	Dioxane	2.7×10^{-1}	45	32	51

[a] The yields of redistilled esters (infrared spectra superimposable on those of authentic esters) are based on the amide used in the two-step process of nitrosation and elimination of nitrogen. In each run, the acids and olefins formed (eq. 1, path b), account for the remainder of the nitrosoamide. [b] Based on the optical activity of the amide; however, this was equal to the activity of the nitrosoamide, since no racemization occurs during the nitrosation step (footnote 40); error, *ca.* ±0.5%. [c] Based on the activity of the amide; error, ±2% for run 15 and ±1% for the others. [d] A volatile, optically inactive impurity was obtained in these runs. It was removed by chromatography on alumina—the pentane eluate yielded the pure ester. In run 10, 8000 mole % of Na_2CO_3 was used, and in runs 4, 5, 7 and 8, 400 mole %. [e] Purified according to L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

indicates that the mechanism of the nitrogen elimination reaction is more complex than outlined in 5, and that the stereochemical course of the reaction is markedly influenced by the solvent used. The gradual trend from inversion to retention of configuration observed in the different solvents, as well as the gradual trend in the composition of the olefin mixtures (eq. 1b) obtained (Table II), suggest, however, that the reaction mechanisms in these solvents differ in degree rather than in kind. For this reason, the following discussion will be concerned largely with the reactions in pentane and in dioxane, the solvents in which the reaction was studied the most thoroughly.

A. The Reaction in Pentane. Inversion.—The occurrence of a bimolecular inversion reaction (eq. 6b) in pentane was shown in several ways: (a) The elimination of nitrogen from (+)N-(*sec*-butyl)-N-nitrosobenzamide in the presence of an excess of benzoic acid yielded *sec*-butyl benzoate with a higher inversion of configuration than that obtained in the absence of the added acid (compare runs 1 and 3). (b) The nitrogen elimination in the presence of sodium carbonate (to remove the benzoic acid as formed) yielded *sec*-butyl benzoate with increased retention of configuration (compare runs 2 and 4 and 9 and 10). (c) The rearrangement in the presence of an added acid ($R''CO_2H$) yielded two esters, $R'CO_2R$ and $R''CO_2R$. The latter was formed with an over-all inversion of configuration (not completely inverted, presumably because interchange of the acyloxy group can occur prior to the nitrogen elimination step—eq. 6d), whereas the former ($R'CO_2R$) was obtained with an enhanced retention of configuration as expected, since the reaction of equation 6b would have been eliminated in favor of that of eq. 6c (compare runs 2 and 6). (d) Dilution would be expected to favor the uni-

CHART I

CONFIGURATIONAL RELATIONSHIPS AND SPECIFIC ROTATIONS OF OPTICALLY PURE INTERMEDIATES

A. L-*sec*-Butyl Derivatives[d]

Amines and derivatives	Alcohols and derivatives
sec-Butylamine tartrate +17.2 at 25° (H_2O)[a] +21.10 at 25° (H_2O)[b]	
sec-Butylamine +7.44 at 20° (neat)[m]	*sec*-Butyl alcohol +13.83 at 21° (neat)[g]
N(*sec*-Butyl)-acetamide +16.6 at 25° ($CHCl_3$)[c]	*sec*-Butyl acetate +25.07 at 20° ($CHCl_3$)[e]
N-(*sec*-Butyl)-benzamide +30.74 at 25° (EtOH)[b]	*sec*-Butyl benzoate +40.38 at 20° (CS_2)[f]
N-(*sec*-Butyl)-3,5-dinitrobenzamide +24.3 at 27° (EtOH)[c]	*sec*-Butyl-3,5-dinitrobenzoate +38.3 at 21° ($CHCl_3$)[g]

B. α-PHENYLETHYL DERIVATIVES OF THE SAME CONFIGURATION[i]

(−)α-Phenylethylamine −40.3 at 22° (neat, d^{22}_4 0.950)[h]	(−)α-Phenylethanol −42.86 at 20° (neat)[j]
(−)N-(α-Phenylethyl)-acetamide −168.1 at 17° (EtOH)[k]	(−)α-Phenylethyl acetate −127.6 at 24° (C_6H_6)[l]

[a] Maximum value obtained. Apparently optically pure, since the salt yielded N-(*sec*-butyl)-benzamide with $[\alpha]^{27}D$ +30.65° (EtOH). [b] N. J. Leonard and E. W. Nommensen, THIS JOURNAL, 71, 2810 (1949). [c] See Experimental section. [d] (+)*sec*-Butylamine has been shown to have the same configuration as (+)*sec*-butyl alcohol (P. A. Levene, A. Rothen and M. Kuna, *J. Biol. Chem.*, 115, 415 (1936) and also footnote L). (+)*sec*-Butyl alcohol has been shown to have the same configuration as L-glyceraldehyde (P. A. Levene and H. L. Haller, *ibid.*, 65, 49 (1925); 67, 329 (1926); 69, 165 (1926); 71, 465 (1927); and K. Freudenberg, *Ber.*, 47, 2027 (1914)). [e] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 105, 830 (1914). [f] J. Kenyon and R. H. Pickard, *ibid.*, 107, 115 (1915). The extrapolated value at 25° was practically the same (neat). [g] Calculated from the data of R. L. Burwell, Jr., THIS JOURNAL, 59, 1609 (1937), and from the $[\alpha]^{21}D$ 13.83° for *sec*-butyl alcohol (J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 137, 1072 (1935)). [h] W. Theilacker and H. G. Winkler, *Ber.*, 87, 690 (1954). [i] (−) α-Phenylethylamine and (−)α-phenylethanol have the same configuration (P. A. Levene, A. Rothen and M. Kuna, *J. Biol. Chem.*, 120, 777 (1937)). [j] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 99, 45 (1911). [k] A. Campbell and J. Kenyon, *ibid.*, 148, 25 (1946). [l] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 97, 379 (1932). [m] L. G. Thomé, *Ber.*, 36, 582 (1903).

molecular reaction leading to retention (eq. 6a) over the bimolecular reaction leading to inversion (eq. 6b). Such a shift to higher retention was observed (compare runs 3 and 9 and 4, 5 and 10). The striking effect of dilution on the course of the reaction, from 8% inversion in run 4 to 13% retention in run 10 (even in the presence of sodium carbonate which would itself decrease the incidence of reaction 6b), suggests that in solvents of low solvating ability, the bimolecular inversion represents an important mode of reaction for the diazo ester.[17,18]

(17) The importance of bimolecular inversion in non-polar solvents may be associated with a solvation of the reacting molecule by the products of the reaction (ester, $R'CO_2R$ and acid, $R'CO_2H$), similar to the solvation which occurs during the reaction in dioxane. A solvation by the acid ($R'CO_2H$) would be expected to lead to an appreciable amount of ester by inversion.

(18) Similarly, at least part of the inversion of configuration observed in the formation of alkyl chlorides from alkyl chlorosulfites (footnote 28) in a number of solvents, may have occurred *via* bimolecular inversion with the hydrogen chloride formed as a by-product. The effect of dilution on the stereochemical course of the reaction, noticed by Cram (F. A. A. Elhafez and D. J. Cram, THIS JOURNAL, 75, 344 (1953)), is then understandable in terms of the unimolecular reaction leading to retention and a bimolecular reaction of the chlorosulfite with hydrogen chloride (or with chloride ion) leading to inversion of configuration.

TABLE II

COMPOSITION OF THE BUTENES FROM THE N-(*sec*-BUTYL)-N-NITROSOAMIDES[a]

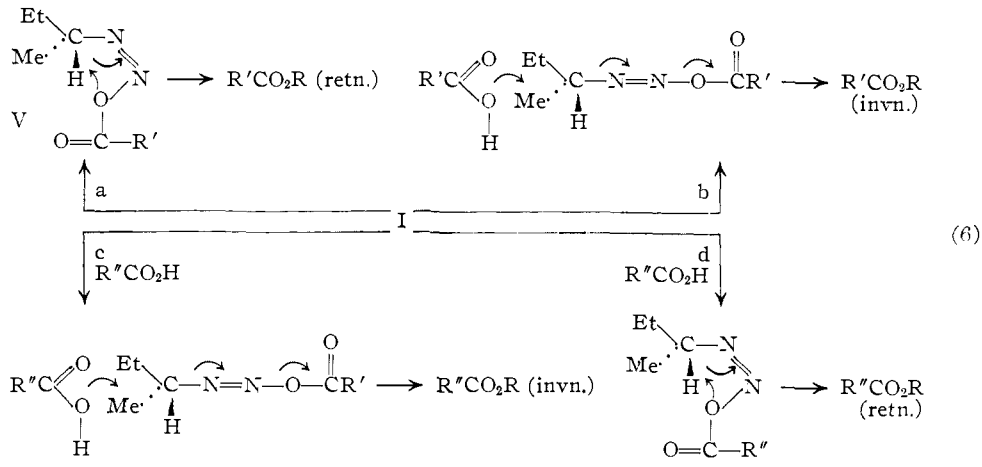
Reactant	Solvent[b]	1-Butene, %	2-Butene, % *trans*	*cis*
N-(*sec*-Butyl)-N-nitrosobenzamide (V)	Heptane (99°)	57	43	
N-(*sec*-Butyl)-N-nitrosoacetamide (VI)[c]	CCl_4	54	33	13
V	Toluene	53	34	13
N-(*sec*-Butyl)-N-nitroacetamide	CCl_4	52	48	
V	Dioxane	49	39	12
V	Acetic acid	45	40	15
VI	Vapor phase (190°)	42	42	16
sec-Butylamine + nitrous acid	Water	26	56	18

[a] Isomer distributions determined from the infrared spectra of carbon tetrachloride solutions of the mixed butenes. Error *ca.* ±2%. [b] Unless specified, temp. 25°. [c] Na_2CO_3 present in this run.

Retention.—The occurrence of a reaction proceeding with retention of configuration is indicated by the results of runs 6–10. That the retention is due to an intramolecular process and not to an intermolecular reaction was shown by the *increase* in retention observed in runs at high dilution (compare runs 2 and 9 and 4, 5 and 10). This reaction is represented in equation 6a.[19] The four-membered transition state for this reaction is similar to that proposed for the reaction of 2-phenylethylamine with nitrosyl chloride, a reaction which yields the corresponding chloride with partial retention of configuration.[20] Some charge separation (stabilized by resonance with the acyl and R groups) probably exists in V (as in IX), since isomerization was observed in the elimination of nitrogen from the analogous normal and isobutyl nitrosoamides in pentane.[2] As expected in pentane, these partial charges must be relatively small since not only were the yields of isomers quite low,[2] but in addition, the isomer distribution was different from that usually observed in reactions in which intermediate ions or ion pairs are formed. For example, the nitrous acid deamination of isobutylamine[2] yields

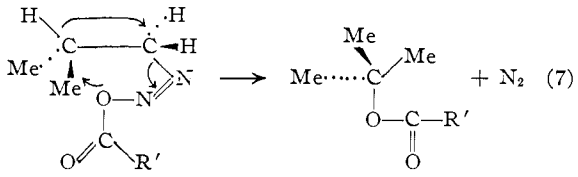
(19) Formation of the diazo ester from the nitrosoamide by a cyclic path (equation 2) would yield the *trans* isomer (see footnote 4 for a discussion of the isomerization of the aryl diazo esters); however, molecular models show that the oxygen atoms of the *trans* isomer are not within bonding distance of the carbon atom undergoing displacement. In all probability, therefore, an isomerization to the *cis* form precedes the nitrogen elimination step. Similar isomerizations in related cases have been established by Le Fevre for azobenzenes (R. J. W. Le Fevre and J. Northcott, *J. Chem. Soc.*, 867 (1953)), for diazo cyanides (R. J. W. Le Fevre and J. Northcott, *ibid.*, 944 (1949)), and for oximes (R. J. W. Le Fevre and J. Northcott, *ibid.*, 2235 (1949)).

(20) H. Felkin, *Compt. rend.*, 236, 298 (1953). Similar reactions may be involved in the nitrous acid and nitrosyl chloride deaminations of 1-aminoapocamphane (P. D. Bartlett and L. H. Knox, THIS JOURNAL, 61, 3184 (1939)).



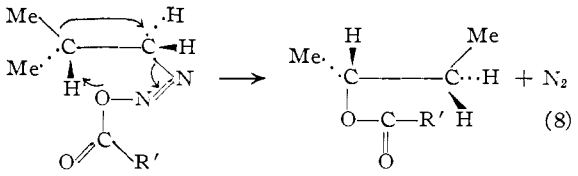
(6)

besides isobutyl alcohol; *t*-butyl alcohol and *sec*-butyl alcohol in the ratio 7/1, a reflection of the relative stabilities of the tertiary and secondary carbonium ions. The elimination of nitrogen from N-(isobutyl)-N-nitroso-3,5-dinitrobenzamide in hexane, however, yields besides the isobutyl ester, the *t*-butyl ester and the *sec*-butyl ester in the ratio of 1/3.5.[2] This inverse ratio in which the isomers are formed suggests that because of the concerted nature of the process, the isomerization in the latter case is sterically controlled. The transition state for the concerted migration of the proton involves approach of the oxygen atom between two methyl groups whereas the transition



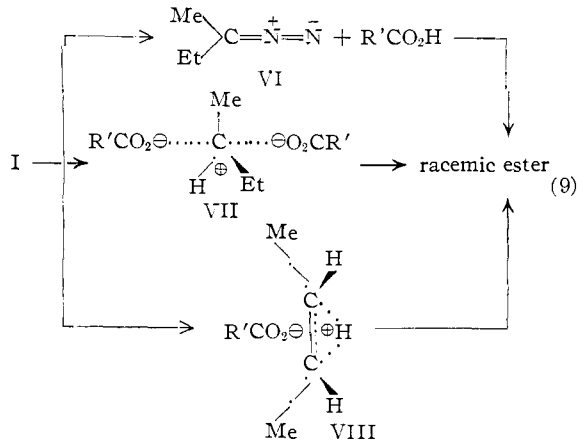
(7)

state for migration of the methyl group involves the sterically more favorable approach between a methyl group and a hydrogen atom.



(8)

Apparent Racemization.—A striking feature of the stereochemical results (Table I) is the considerable loss of optical activity which has occurred in the nitrogen elimination step. This loss of activity can be accounted for either by a true racemization[21] or by an apparent racemization, *i.e.*, a combination of reactions proceeding with retention of configuration and those proceeding with inversion of configuration. The following experimental results indicate that the former explanation is incorrect. Although the results in pentane solutions are qualitative in nature, the evidence obtained from runs in dioxane is quite conclusive (*vide infra*). Various possible inactive intermediates[22] required for the true racemization are listed in eq. 9.

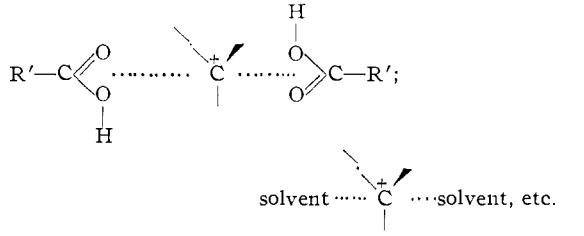


(9)

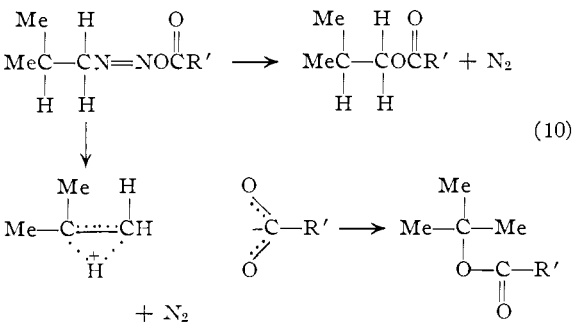
Under the reaction conditions used, it is unlikely that the bridged ion VIII could have been responsible for the racemization observed. Roberts[23] has shown that bridged ions play a negligible role in the nitrous acid deamination in aqueous solution; in the relatively non-polar solvents used in the nitrogen elimination from I, this ion VIII should be even less important. In addition, in a related case where ions such as VIII would be expected to react by proton migration (the isobutyl analog) less than 1% of the product consisted of the *t*-butyl ester[2] (eq. 10).

(21) True racemization may be defined as the loss of optical activity during a reaction due to the formation of an intermediate incapable of supporting optical activity.

(22) Equation 9 is intended as a general equation for racemization in all of the solvents used. In pentane, specifically, the formation of the ion VII would be rather unlikely. The acid necessary for VII is formed in all of the rearrangements *via* path b, eq. 1. The evidence concerning the unimportance of VII in this reaction applies equally well to other symmetrical ions—



(23) J. D. Roberts and J. A. Yancey, THIS JOURNAL, **74**, 5943 (1952).



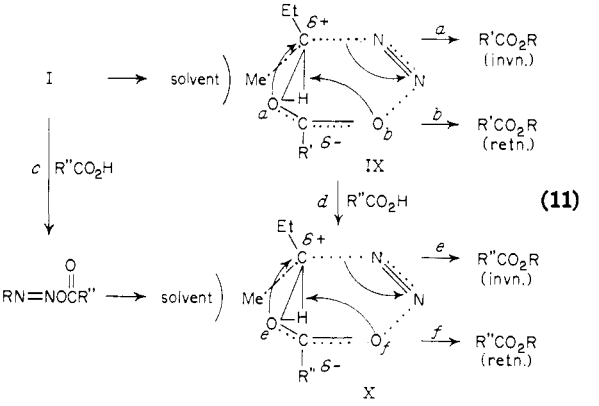
(10)

Concerning the intermediates VI and VII (eq. 9); in the presence of an excess of an added acid ($R''CO_2H$), VII would be replaced by $R''CO_2^-$.....$\overset{+}{C}$.....O_2CR'', and both this ion and VI should yield a new ester ($R''CO_2R$) in amounts ranging from *ca.* 59% of the total ester in run 17 to *ca.* 98% in run 5. This new ester should be inactive, whereas the normal ester ($R'CO_2R$) should, under these conditions, show an enhanced activity. Experimentally, the rearrangement of I in the presence of an added acid yielded results which were inconsistent with this picture. Run 2 can be considered the normal run (89% loss of optical activity). In the presence of $R''CO_2H$ (run 6), the normal ester ($R'CO_2R$) was even less active than that from run 2; the new ester ($R''CO_2R$) accounted for only 30% of the total ester obtained, and was itself relatively highly active. Furthermore, in the presence of solid sodium carbonate,[24] the formation of VII would be disfavored and the formation and accumulation of VI would be favored[25]—in either case less racemization should be observed in the ester. Experimentally, the ester obtained from certain runs with sodium carbonate was more racemic (compare runs 3 and 5). In addition, the diazoalkane VI was never observed in infrared spectra of the reaction mixtures.[26]

That part of the racemic ester did not arise from recombination of the acid and olefin formed in the elimination reaction (eq. 1, path b), was shown by subjecting a mixture of 1-butene, 2-butene and 3,5-dinitrobenzoic acid to the reaction conditions usually employed. Not a trace of ester was detected (infrared spectra).

The loss of activity observed (Table I) therefore must be attributed to an apparent racemization, *i.e.*, a combination of reactions 6a and 6b, and possibly others. The response of the optical activity of the ester to the concentration of benzoic acid (required for the bimolecular inversion) was sufficiently small (compare runs 1, 3 and 5) to suggest that another process leading to inversion is operative. In addition, nitrogen elimination at high dilution in the presence of sodium carbonate (conditions which should practically eliminate the bimolecular inversion) yielded an ester which showed only a low retention of configuration (run 10). In all probability, therefore, the intramolecular inversion reaction proposed for the dioxane runs (eq. 11) occurs in pentane as well, and along with reaction 6a would account for the low activity observed, *e.g.*, in run 10.

B. The Reaction in Dioxane.—The nitrogen elimination from I in dioxane in the presence of an excess of an added acid $R''CO_2H$ (to compete with the $R'CO_2H$ formed in the elimination reaction, eq. 1b) yielded two esters, $R''CO_2R$ and $R'CO_2R$. Both showed approximately the same retention of configuration (run 18), which in the case of the latter ester was the same as that observed in the absence of $R''CO_2H$. These results indicate that in dioxane: (a) bimolecular inversion (eq. 6, b and c) does not occur,[27] (b) true racemization does not occur (section A), and (c) acid interchange occurs, prior to the nitrogen elimination step. The loss of optical activity observed (runs 16, 17 and 18) must be due, therefore, to an apparent racemization—in this case, a combination of intramolecular retention and intramolecular inversion reactions.[28] The absence of the intermolecular inversion reaction (an important reaction in pentane solutions, equation 6b,c) suggests that dioxane solvates the asymmetric carbon atom, preventing the rearward approach of an acid molecule. The presence of such effective solvation in turn suggests that during the nitrogen elimination step, intermediates with appreciable charge separations are formed. The proposed mechanism is given in eq. 11. Molecular models arranged[29] as in IX show that oxygen atom



(11)

(24) Under the reaction conditions used, the free acid was completely neutralized by the carbonate. In non-polar solvents, the sodium carbonate had no effect on either the yields or on the isomer distribution.[2]

(25) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1059 (1939). In this case, cyclohexanone was added to react with the diazoalkane as formed.

(26) Diazo alkanes were obtained from more favorably substituted compounds (with the nitrosoacylamide group attached to a carbon bearing an active hydrogen), *i.e.*, methyl N-benzoyl-N-nitrosoalanate yielded methyl α-diazopropionate (footnote 2). In all probability the stilbene (but not the benzyl acetate) obtained from N-benzyl-N-nitrosoacetamide in the presence of potassium carbonate (W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934)), was formed from the intermediate phenyldiazomethane.

(27) The non-occurrence of intermolecular inversion in dioxane solutions was also shown by the independence of the concentration and the stereochemical course of the reaction (runs 17 and 16). Dilution should favor an intramolecular reaction over an intermolecular reaction, an effect noted in the rearrangements in pentane solutions.

(28) C. E. Boozer and E. S. Lewis, THIS JOURNAL, **75**, 3182 (1953), have proposed an intramolecular inversion process for the formation of alkyl chlorides from alkyl chlorosulfites in toluene.

(29) In order to achieve coplanarity in the models, *ca.* 25% bond stretching is required for the carbon–nitrogen and nitrogen–oxygen bonds. Coplanarity would be aided by the resonance stabilization of the partial positive charge, which would presumably increase slightly the carbon–nitrogen–nitrogen bond angle.

b is well situated for a front side displacement of nitrogen to form the ester with retention of configuration. Oxygen atom a lies slightly behind the plane of the asymmetric carbon atom and can displace nitrogen with inversion of configuration. The ratio of a/b must equal the ratio e/f, since both $R'CO_2R$ and $R''CO_2R$ were obtained with *ca.* 40% retention of configuration (run 18). (That the 3,5-dinitrobenzoate ($R''CO_2R$) did not arise by acid interchange with either the nitrosobenzamide or the butyl benzoate was shown by experiment.) The correspondence of the optical activities of the two esters implies that both have similar precursors, *i.e.*, IX and X.[30]

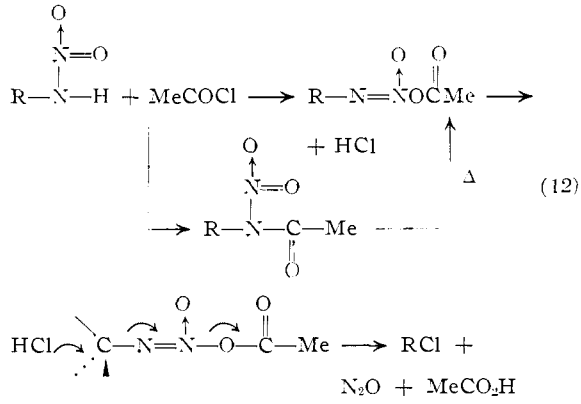
The solvation indicated in IX and X apparently does not involve partial covalent bonding with a single molecule of solvent (in the manner described by Doering and Zeiss[31] for an ion and solvent) since the normal ester ($R'CO_2R$) was obtained with approximately the same stereochemical results in a wide variety of solvents ranging from toluene to acetic acid (runs 11, 12, 13, 14, 15 and 16). Appreciable bonding by the solvent in run 14 (acetic acid) would be expected to lead to considerably more acetate than was actually observed. In addition, compared to dioxane, both pyridine (more basic) and dimethyl sulfide (more nucleophilic) as solvents, proved less able to shield the asymmetric carbon atom from attack by the added acid ($R''CO_2H$), *i.e.*, the new esters ($R''CO_2R$) were considerably more inverted in configuration than the normal esters ($R'CO_2R$) (runs 13 and 15) or the corresponding ester from the dioxane run.

C. The Reaction in Acetic Acid.—Based on configurational changes, the mechanism of the rearrangement in acetic acid is similar to that given for dioxane, since the elimination of nitrogen from (+)N-(*sec*-butyl)-N-nitrosobenzamide in acetic acid yielded *sec*-butyl benzoate ($R'CO_2R$) with a retention of configuration practically the same as that observed from the same reaction in dioxane (runs 14 and 17). Since the solvent (acetic acid, $R''CO_2H$) can participate by inversion (equation 6c) as well as by solvation in this case, the butyl acetate ($R''CO_2R$) was formed with an over-all inversion of configuration (run 14). By the criterion of isomerization, however, the reaction in acetic acid is considerably different from that in dioxane, *i.e.*, in a related case in which isomerization can be observed (the rearrangement of N-(isobutyl)-N-nitroso-3,5-dinitrobenzamide), the butyl 3,5-dinitrobenzoates were obtained with an isomer distribution of iso/*sec*/*tert* equal to 91/8/1 in dioxane and 45/15/40 in acetic acid.[2] The latter isomer ratio approaches that observed in the deamination of isobutylamine with aqueous nitrous acid,[2] suggesting that the rearrangement of nitrosoamides in acetic acid involves intermediates in which considerably greater charge separations[30] occur, compared to the corresponding intermediates in dioxane (IX and X). Apparently, in suitable cases, the amount and type of positional isomerism may give more insight into the mechanism of the reaction than the amount of optical isomerism.

In an attempt to determine the course of the reaction in the absence of solvent, the rearrangement of (+)N-(*sec*-butyl)-N-nitrosoacetamide was carried out in the vapor phase. However, with the contact times available, a temperature of 190° was required for complete elimination of nitrogen. At this temperature, the reaction proceeded almost exclusively by elimination (eq. 1, path b), an extreme case of the effect of an increase in temperature noted in the solvents studied earlier.[2]

The Nitrogen Elimination from N-(α-Phenylethyl)-N-nitrosoacetamide.—The results for the elimination of nitrogen from (+)N-(α-phenylethyl)-N-nitrosoacetamide in pentane, carbon tetrachloride and dioxane are reported in Table I, part B. The results indicate that the rearrangement in this case is relatively independent of the solvent and that a higher retention of configuration is obtained, compared to the rearrangement of (+)N-(*sec*-butyl)-N-nitrosobenzamide (Table I). The phenyl group apparently preferentially favors the retention process over the intermolecular inversion reaction, largely responsible for the solvent effect with the *sec*-butyl analog (possibly by stabilizing the positive charge placed on the asymmetric carbon during the intramolecular reaction (IX, equation 11)). This influence of the phenyl group in favoring retention processes has been noted before in reactions of α-phenylethanol with hydrogen bromide[32] and with thionyl chloride[33]; and under certain conditions, in the nitrous acid deamination of α-phenylethylamine.[34]

N-Nitro Analogs.—The rearrangement of (+)N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide yielded nitrous oxide and optically active *sec*-butyl 3,5-dinitrobenzoate. The configurational changes which occurred (Table I, part B) were sufficiently similar to those obtained with the corresponding nitroso-



(12)

(30) In contrast to the mechanism given in equation 11, a Referee has proposed that a mechanism involving ion-pair intermediates (electrostatic bonding) can account more satisfactorily for the characteristics of the nitrogen elimination step. The author believes, however, that although this may be the case for the reaction in acetic acid (intramolecular—extensive isomerization) the reaction in the other solvents used (intramolecular—little isomerization) is better represented by the more concerted mechanism (eq. 11). Experiments with oxygen-18 labeled nitrosoamides are planned in order to determine more precisely the nature of this reaction.

(31) W. von E. Doering and H. H. Zeiss, THIS JOURNAL, **75**, 4733 (1953).

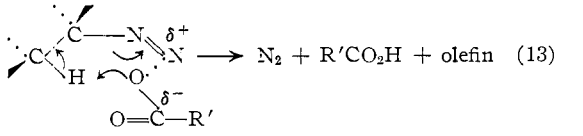
(32) P. A. Levene and A. Rothen, *J. Biol. Chem.*, **127**, 237 (1939); C. L. Arcus, *J. Chem. Soc.*, 236 (1944); see also footnote 14, p. 1252.

(33) J. Kenyon, A. G. Lipscomb and H. Phillips, *ibid.*, 415 (1930).

(34) E. Ott, *Ann.*, **488**, 186 (1931). Compare with the aliphatic analogs, C. K. Ingold, *et al.*, *Nature*, **166**, 179 (1950).

amide to confirm the view that the mechanisms of the two reactions are similar in nature (eqs. 2 and 4). The reaction of acetyl chloride with a nitroamine to yield the corresponding alkyl chloride has been reported recently.[35] This transformation can be satisfactorily accounted for in terms of the reactions reported in the previous sections.

Mechanism of the Olefin Formation (Eq. 1b).—The reaction leading to olefin is intramolecular, since the olefin yields are not altered by the presence of bases such as sodium carbonate[2] (Table I, runs 2, 3, 4 and 5) or pyridine (run 15, see also footnote 2, Table II, run 19) or by acids (run 1). The elimination reaction can then be represented by equation 13.[36] That the reaction is not completely con-



$$\longrightarrow N_2 + R'CO_2H + \text{olefin} \quad (13)$$

certed is shown by the olefin distribution found in various solvents (Table II), *i.e.*, the distribution in the more polar solvents approaches that observed in the deamination of *sec*-butylamine with nitrous acid, a reaction which is usually considered to proceed *via* ionic intermediates.

Experimental

Reaction of 3,5-Dinitrobenzoyl Chloride with the Sodium Salt of N-Nitrobutylamine (IV, R = *n*-Butyl).—N-Nitro-N-(*n*-butyl)-acetamide[2] was saponified and the N-nitrobutylamine[37] liberated, using the procedures of Bachmann.[38] The nitroamine was neutralized with a stoichiometric quantity of sodium hydroxide (aqueous), the solution was evaporated to dryness, and the salt dried for two days at 0.1 mm. The sodium salt (0.172 g., 1.23 mmoles) was added to a solution of 0.283 g. (1.23 moles) of 3,5-dinitrobenzoyl chloride in chloroform (20 ml.); nitrous oxide and butene were evolved. After 2 hr., the solution was washed with aq. sodium carbonate (5%) to remove the 3,5-dinitrobenzoic acid (path b, eq. 1). The chloroform was removed at reduced pressure and the residue extracted with pentane to yield *n*-butyl 3,5-dinitrobenzoate (25%). The residue was N-nitro-N-(*n*-butyl)-3,5-dinitrobenzamide (30%). The products were purified by chromatography, and identified by their infrared spectra.[39]

Experimental Evidence Excluding Free Radical Intermediates.—(i) N-(*sec*-Butyl)-benzamide (1.08 g., 6.11 mmoles) was nitrosated with nitrogen tetroxide in carbon tetrachloride by the procedure given in Part I.[40] The carbon tetrachloride solution of the nitrosoamide was evaporated under reduced pressure at 0°, and the yellow oil (pure N-(*sec*-butyl)-N-nitrosobenzamide, as shown by the infrared spectrum) was dissolved in redistilled styrene (20 ml.). The solution was allowed to stand at 25° for 5 hr., then warmed to 60° for 0.5 hr. (The evolution of nitrogen had ceased.) The styrene was then distilled from the ester at 0.1 mm. (redistillation yielded only styrene, b.p. 48–49° at 25 mm.). The residue was dissolved in pentane, and the solution titrated with 0.1 *N* sodium hydroxide (35.3 ml. req., 3.53 mmole = 58% benzoic acid). The pentane solution was dried, the pentane removed, and the *sec*-butyl benzoate distilled (0.0992 g., 0.558 mmole, 9.1%)—only a slight trace of residue remained. The yields given are based on the starting amide, and thus represent over-all yields for the two steps. The infrared spectrum of the ester was superimposable on that of an authentic sample of *n*-butyl benzoate.

(ii) A stream of nitric oxide was passed into a refluxing 0.03 *M* solution of N-(isobutyl)-N-nitroso-3,5-dinitrobenzamide[40] in carbon tetrachloride (previously flushed with N_2) for 5 hr. The products were identical to those obtained in the absence of nitric oxide[2] (both yields and infrared spectra). A similar experiment with N-(*sec*-butyl)-N-nitrosobenzamide (which normally yields *ca.* 65% 1-butene and 25% ester)[2] at 25° yielded nitrogenous products which were identical, however, to those obtained from the reactions of nitric oxide with a mixture of 1-butene and benzoic acid.

(iii) Gas samples were taken from most of the nitrogen elimination reactions reported earlier.[2] Neither of the absorption bands (4.30 and 14.98 μ) characteristic of carbon dioxide were found in any of the infrared spectra of these gas samples.

Procedures Used for the Runs of Table I.—Samples of the optically active amides were nitrosated with nitrogen tetroxide[40] and rearranged in the appropriate solvent.[2]

That racemization does not occur during the nitrosation step had been shown by the nitrosation of an optically active amide and subsequent denitrosation to yield the regenerated amide with undiminished rotation.[40] In each run (Table I), the acid was neutralized and the solvent distilled through a small column. The *sec*-butyl acetate was distilled from the remaining products at atmospheric pressure, then redistilled. The *sec*-butyl benzoate was removed at 0.05 mm. and 75°, then redistilled. The remaining *sec*-butyl 3,5-dinitrobenzoate (in runs 11, 13 and etc.) was chromatographed on acid-washed alumina (activated at 200° for 10 hr.). The column was washed with pentane, then the pure ester eluted with ether. In run 18 the ester was then recrystallized from pentane at −60°. In run 19 the ester was pure (infrared spectrum) and chromatography was not employed. The α-phenylethyl acetate was purified by distillation. The various separations were carried out as quantitatively as possible in order to prevent fractionation of the active and racemic forms. The rotations were taken in a 1-dm. water-jacketed polarimeter tube. In a typical run (run 17) N-(*sec*-butyl)-benzamide, $\alpha^{25}D$ +1.115 ± 0.005°, $[\alpha]^{25}D$ +19.84° (0.1124 g. dil. to 2 ml. with absolute ethanol), 64.6% optically pure, was converted to the nitrosoamide[41] and rearranged.[2] The *sec*-butyl benzoate was obtained with $\alpha^{25}D$ +0.676 ± 0.007°, $[\alpha]^{25}D$ +10.62° (0.1272 g. dil. to 2 ml. with CS_2), 26.3% optically pure.

Preparation of Optically Pure Derivatives (Chart I).—*sec*-Butylamine was resolved by the method of Thomé.[42,43] Leonard reports $[\alpha]^{25}D$ +21.10° (*c* 4.1 in H_2O) for the optically pure bitartrate, whereas $[\alpha]^{25}D$ +17.1° (*c* 5.26 in H_2O) was observed in this Laboratory.[44] That the tartrate (17.1°) was optically pure, was shown by preparing N-(*sec*-butyl)-benzamide from it. The observed value of $[\alpha]^{27}D$ +30.65° (*c* 7.00 in EtOH) checks well with that reported for the optically pure benzamide by Leonard,[42] $[\alpha]^{25}D$ +30.74° (*c* 4.0 in EtOH). The N-(*sec*-butyl)-3,5-dinitrobenzamide prepared from the same tartrate had $[\alpha]^{25}D$ +24.3 (*c* 2.29 in EtOH). *sec*-Butylamine $[\alpha]^{20}D$ +4.99°, 67.1% (optically pure) was converted into N-(*sec*-butyl)-acetamide, $[\alpha]^{25}D$ +11.12° (*c* 6.06 in $CHCl_3$). The extrapolated value for the optically pure acetamide would then be $[\alpha]^{25}D$ +16.6° ($CHCl_3$).

The α-phenylethyl derivatives were prepared according to the references given in Chart I. The preparation of (+) (*sec*-butyl)-N-nitro-3,5-dinitrobenzamide will be reported elsewhere.[39]

(35) R. H. Hall and G. F. Wright, THIS JOURNAL, **73**, 2208 (1951); A. F. McKay and W. G. Hatton, *ibid.*, **75**, 963 (1953), and leading references.

(36) The diazo ester is probably a common precursor for both ester and olefin, *i.e.*, preliminary studies have shown that the over-all rate of nitrogen evolution is identical to the rate of acid formation (first order reactions). Both reactions, therefore, have a common rate-determining step—the rearrangement of the nitrosoamide into the diazo ester (eq. 2).

(37) H. Van Erp, *Rec. trav. chim.*, **14**, 26 (1895); J. W. Brühl, *Z. physik. Chem.*, **22**, 388 (1897).

(38) W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and C. E. Maxwell, THIS JOURNAL, **72**, 3132 (1950).

(39) This and a number of similar reactions in the nitro series will be reported in detail at a later date.

(40) E. H. White, THIS JOURNAL, **77**, 6008 (1955).

(41) Using method E, see footnote 40.

(42) L. G. Thomé, *Ber.*, **36**, 582 (1903); see also Leonard, THIS JOURNAL, **71**, 2810 (1949).

(43) A convenient modification of Thomé's method consists of allowing an aqueous solution of the amine tartrate to evaporate slowly. The first crop (20%) is 70% optically pure (+).

(44) The tartrate analyzed for the 1/1 salt-monohydrate. *Anal.* Calcd. for $C_8H_{19}NO_7$: C, 39.83; H, 7.94; N, 5.81. Found: C, 39.54; H, 7.98; N, 5.93.

Attempted Reaction of 1-Butene with 3,5-Dinitrobenzoic Acid.—A slow stream of 1-butene was passed through a saturated solution of the acid in toluene for six hours. The mixture was poured into water, the mixture extracted with ether, the ether washed with aq. sodium hydroxide (5%) and the ether dried and evaporated. The infrared spectrum of the trace of residue was devoid of bands in the carbonyl region.

Ester Interchange Experiments.—One gram of isobutyl 3,5-dinitrobenzoate was dissolved in 15 ml. of glacial acetic acid at 25°. After three days, the solution was poured into water, the esters extracted with ether, the ether solution washed with aqueous sodium carbonate (5%), the ether dried and evaporated, and the residue held at 100° and 0.01 mm. for one hr. (to remove the volatile acetate). The residue weighed 0.97 g. (97%) and the infrared spectrum was identical with that of pure isobutyl 3,5-dinitrobenzoate. In a similar experiment (with acetic acid as solvent (115° for one hour)), 94% of the isobutyl 3,5-dinitrobenzoate was recovered.

The nitrosoamides apparently do not undergo acyl interchange, since N-nitroso-3,5-dinitrobenzamides can be prepared in 95% yield from the corresponding amides and nitrogen tetroxide[40] in acetic acid.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

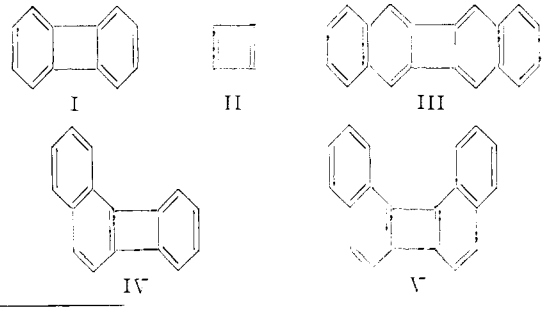
Condensed Cyclobutane Aromatic Systems. I. The Synthesis of 1,2-Benzobiphenylene and 1,2-Binaphthylene[1]

BY M. P. CAVA AND J. F. STUCKER

RECEIVED MAY 17, 1955

Two new benzo derivatives of biphenylene, 1,2-benzobiphenylene (IV) and 1,2-binaphthylene (V), have been synthesized using 1-(2-aminophenyl)-2-naphthylamine (VI) and 2,2′-diamino-1,1′-binaphthyl (XVI), respectively, as starting materials. Some chemical and physical properties of these hydrocarbons are described.

The hydrocarbon biphenylene (I) is a substance of considerable theoretical interest since it may be considered as the dibenzo derivative of the unknown and elusive cyclobutadiene (II). Biphenylene has been prepared by three different methods: (1) pyrolysis of 2,2′-dibromobiphenyl or, better, of biphenyleneiodonium iodide with cuprous oxide,[2] (2) treatment of the Grignard reagent of 2,2′-dibromobiphenyl with cupric chloride[3] and (3) pyrolysis of biphenylyl mercury with silver powder.[4] Although several substitution products of biphenylene are known,[5] only one other polynuclear aromatic system has been reported which contains a cyclobutadiene nucleus, that is, 2,3,6,7-dibenzobiphenylene or 2,3-binaphthylene (III).[6] As a part of a general program to prepare other such systems, we have now synthesized 1,2-benzobiphenylene (IV) and 1,2,7,8-dibenzobiphenylene or 1,2-binaphthylene (V).



The starting material for the preparation of IV was 1-(2-aminophenyl)-2-naphthylamine (VI), which is obtained as a by-product in the preparation of 1,2-benzocarbazole from 2-naphthol and phenylhydrazine in the presence of sulfur dioxide.[7] In spite of its indirect mode of formation, the structure of this diamine is known with certainty because of its conversion to 1,2-benzocarbazole by sulfurous acid, and by its deamination to[7] 1-phenylnaphthalene (VII). Tetrazotization of VI in the usual manner gave a solution which reacted with sodium iodide to produce a 12% yield of crude 1,2-benzobiphenyleneiodonium iodide (VIII) as well as a 17% yield of 1-(2-iodophenyl)-2-iodonaphthalene (IX). When the iodonium iodide was pyrolyzed with cuprous oxide under the general conditions used to prepare biphenylene itself[5b] IV could be isolated in 6% yield as its black, sparingly soluble 2,4,7-trinitrofluorenone complex X. Pyrolysis of the diiodide IX in the same manner gave a product from which the same complex X was prepared in 63% yield, a remarkably high yield for the formation of a biphenylene type system. The exact nature of the cuprous oxide used was found to be a critical factor in the reaction. High yields were obtained only with one particular lot of Baker C.P. reagent, and with a sample prepared by the hydrazine reduction of cupric acetate.[8]

The diiodide IX reacted readily with lithium to give a solution of the dilithium derivative XI. The addition of mercuric chloride to this solution gave, in 65% yield, 3,4-benzobiphenylylmercury (XII). When XII was heated to 360° with silver powder a sublimate was produced from which, after treatment with 2,4,7-trinitrofluorenone, the black X was obtained in 17% yield.

Regeneration of the free hydrocarbon from X by chromatography on alumina gave an essentially quantitative recovery of pure IV as bright yellow

(1) From the M.S. thesis of J. F. Stucker, The Ohio State University, 1955. A preliminary note concerning 1,2-binaphthylene has appeared in *Chem. and Ind.*, 446 (1955). The remainder of this work was presented before the Division of Organic Chemistry at Cincinnati, Ohio, March, 1955.

(2) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).

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