Tetrahedron, 1965, Vol. 21, pp. 2735 to 2742. Pergamon Press Ltd. Printed in Northern Ireland

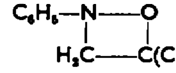
FORMATION OF ACYCLIC PRODUCTS IN THE REACTIONS OF DIETHYL METHYLENEMALONATE AND 1,1-DIPHENYLETHYLENE WITH NITROSOBENZENE[1]

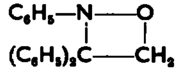
C. E. Griffin, N. F. Hepfinger[2]
Department of Chemistry, University of Pittsburgh, Pennsylvania
and
B. L. Shapiro[2]
Mellon Institute, Pittsburgh, Pennsylvania

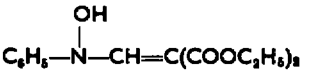
(*Received* 17 *March* 1965)

Abstract—A reinvestigation of the reactions of nitrosobenzene with diethyl methylenemalonate and 1,1-diphenylethylene has shown that the products obtained are N-phenyl-N-(β,β-dicarbethoxyvinyl)-hydroxylamine and α,α,N-triphenylnitrone, respectively. These findings refute the previous assignments (Ingold, 1924) of 1,2-oxazetidine ring structures for these products. Proofs of structure were based upon IR, UV and PMR spectroscopy in addition to degradation and reduction studies.

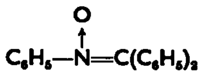
The formation of the 1,2-oxazetidine ring system by the cycloaddition of fluorinated olefins to nitroso compounds, e.g. tetrafluoroethylene and trifluoronitrosomethane, has been shown to be a general reaction by the studies of Haszeldine.[3] In 1964, the formation of 2-phenyl-3,3,4,4-tetramethoxy-1,2-oxazetidine by the cycloaddition of nitrosobenzene (I) to tetramethoxyethylene was reported.[4] Prior to this report, the only examples of non-halogenated oxazetidines recorded in the literature were reported by Ingold and Weaver[5] in 1924. The adducts of I with diethyl methylenemalonate (II) and 1,1-diphenylethylene (III) were assigned structures IV and V, respectively, by these investigators. In 1925, these structural assignments were challenged by Lapworth,[6] who, on the basis of degradation and synthetic studies, proposed the alternative structures VI and VII. The postulation of acyclic structures


IV


V


VI

$C_6H_5-\overset{OH}{\overset{|}{N}}-CH{=}C(COOC_2H_5)_2$


VII

$C_6H_5-\overset{O}{\overset{\uparrow}{N}}{=}C(C_6H_5)_2$

---

[1] Preliminary communication: *Tetrahedron Letters* 1365 (1963). This study was supported in part by a grant (RG 6811) from the Division of General Medical Sciences, U.S. Public Health Service.

[2] Present addresses: NFH, Celanese Corporation of America, Summit, New Jersey; BLS, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

[3] D. A. Barr, R. N. Haszeldine and C. J. Willis, *J. Chem. Soc.* 1351 (1961) and earlier papers.

[4] R. W. Hoffmann and H. Hauser, *Ang. Chem. Int. Ed. Eng.* **3**, 380 (1964).

[5] C. K. Ingold and S. D. Weaver, *J. Chem. Soc.* **125**, 1456 (1924).

[6] G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.* **127**, 1748 (1925); G. N. Burkhardt, A. Lapworth and J. Walkden, *Ibid.* **127**, 2458 (1925).

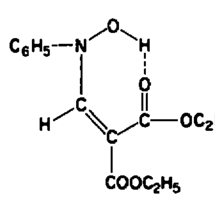
is in accord with the earlier studies of Alessandri[7] of the reactions of nitrosobenzene with olefins. Alessandri showed that vinyl-benzenes underwent reaction with I to form α,N-diphenylnitrones, the terminal carbon of the olefin being cleaved during the process. Allylbenzenes underwent reaction with I without cleavage to form nitrones retaining the original carbon skeleton of the olefin.

Unfortunately, the Lapworth critique was abstracted obscurely and has been overlooked by more recent workers in this field[8] and the conclusions of Ingold and Weaver have been generally accepted. As part of a general study of the reactions of nitrosobenzene with mono- and di-enic systems,[9] the reactions of I with II and III have been reinvestigated and the structural assignments of Lapworth have been confirmed.

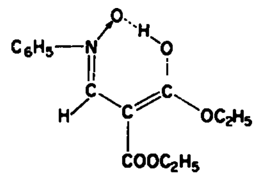
Diethyl methylenemalonate and nitrosobenzene

The reaction of I and II was carried out in refluxing chloroform solution following the procedure of Ingold and Weaver.[5] The chemical and physical properties of the isolated product were identical to those reported[5,6] and an elemental analysis consistent with the isomeric structures IV and VI was obtained. The IR spectrum of the adduct showed a broad hydrogen bonded hydroxyl absorption at 3215 cm^{-1} in addition to absorptions characteristic of ester carbonyl (1701 cm^{-1}) and olefinic (1600 cm^{-1}) functions.[10] These absorptions are consistent only with the assignment of structure VI to the adduct. Further support for this structural assignment was provided by the UV spectrum of the adduct which showed maxima at 224 and 317 mμ, indicative of a more extended chromophoric system than expected for structure IV. The oxazetidine IV would be expected to show the typical absorption of an anilino chromophore (230 and 280 mμ).[11]

Unequivocal confirmation of the structure was provided by the PMR spectrum of the adduct. Resonances characteristic of all of the structural features of VI were observed, i.e. (a) A sharp one proton singlet at $\tau = -2{\cdot}46$ assignable to the strongly hydrogen-bonded hydroxyl proton as in structure VIa. The precise chemical shift for



VIa



VIb

---

[7] [a] L. Alessandri, *Gazz. chim. Ital.* **54**, 426 (1924) and earlier papers; [b] J. Hamer and A. Macaluso, *Chem. Revs.* **64**, 473 (1964).

[8] B. G. Gowenlock and W. Luttke, *Quart. Revs.* **12**, 321 (1958); J. Hamer and A. Macaluso, *Tetrahedron Letters* 381 (1963).

[9] [a] C. E. Griffin, N. F. Hepfinger and B. L. Shapiro, *J. Amer. Chem. Soc.* **85**, 2683 (1963); [b] N. F. Hepfinger and C. E. Griffin, *Tetrahedron Letters* 1361 (1963).

[10] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Second Edition) J. Wiley, New York, N.Y. (1958).

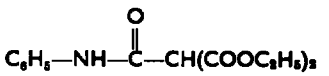
[11] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy* (Second Edition) Arnold, London (1958).

protons of this type depends upon the strength of the hydrogen bond such that the hydrogen bonded enolic or phenolic proton resonances of bis-(*p*-bromobenzoyl)-methane, ethyl *p*-methylbenzoylacetate, 2-thienyl-1,1,1-trifluoroacetone and 4-isopropylsalicylaldehyde occur at $\tau = -6{\cdot}61$, $-5{\cdot}33$, $-4{\cdot}17$ and $-1{\cdot}00$, respectively.[12] (b) A one proton singlet at $\tau = 1{\cdot}62$, a reasonable chemical shift for the olefinic proton in view of its position at the highly electron deficient terminus of the α,β-unsaturated carbonyl system. The α-proton signals of 2,3-dimethoxy-β-nitrostyrene and β,β-dicyano-2-methylstyrene are found in this region ($\tau = 1{\cdot}79$–$1{\cdot}80$).[12] Moreover, the attachment of the electronegative nitrogen to the olefinic carbon atom would also contribute to the deshielding of the olefinic proton. (c) A complex, but well resolved, five proton absorption in the region $\tau = 2{\cdot}58$, assigned to the aromatic protons of the phenyl group attached to tertiary nitrogen, e.g. acetoacetanilide has aromatic absorptions centering at $\tau = 2{\cdot}6$.[12] Studies of model compounds carried out in these laboratories indicate that the small observed internal shifts of the aromatic proton resonances of VI strongly favors formulation VIa over the inherently less likely isomer VIb. In structures analogous to VIb, the *ortho*-proton resonances are shifted considerably more from the *meta*- and *para*-proton resonances.[13] (d) A pair of quartets at $\tau = 5{\cdot}66$ and $5{\cdot}78$ and a pair of triplets at $\tau = 8{\cdot}63$ and $8{\cdot}71$ (total relative intensities: 4 and 6; all $J_{HH} = 7{\cdot}0 \pm 0{\cdot}2$ c/s), clearly indicative of the presence of two magnetically nonequivalent ethoxyl groups attached to some additional unsaturated linkage. The corresponding resonances for diethyl maleate occur at $\tau = 5{\cdot}72$ and $8{\cdot}70$.[12]

The spectral data cited are consistent in all respects (peak positions, splitting patterns and integrated intensities) with the assigned structure VI and the structure proposed by Lapworth is confirmed.[14] The vinylhydroxylamine VI represents the first reported example of a non-nitronic product formed by the reaction of I and a simple mono-olefin.[7]

Lapworth[6] reported that VI could be obtained by the reaction of N-phenylhydroxylamine and diethyl hydroxymethylenemalonate. The observation was confirmed; the samples of VI prepared by the two routes were identical in all respects.

Ingold and Weaver[5] also reported that the adduct of I and II underwent thermal decomposition to yield dicarbethoxy acetanilide (VIII).



$$C_6H_5\text{—NH—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}CH(COOC_2H_5)_2$$

VIII

The formation of a product such as VIII by thermolysis of IV is highly unlikely since Haszeldine[3] has shown that 1,2-oxazetidines decompose thermally to yield azamethines and carbonyl compounds. The formation of VIII by thermal rearrangement of VI appeared to us inherently less likely than other thermal transformations. A material (IX) showing the physical properties reported for VIII was obtained by

---

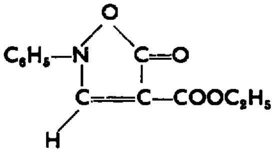
[12] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectra Catalog* Vol. I. Varian Associates, Palo Alto, California (1962).

[13] A more detailed account of these two types of spectra will be published separately.

[14] Based on the work of Alessandri[7a] and the results obtained in this study on the reaction of I and III, two nitronic formulations [$C_6H_5N(O)\!=\!C(COOC_2H_5)_2$ and $C_6H_5N(O)\!=\!CHCH(COOC_2H_5)_2$] were considered as alternative structures for the adduct of I and II. Both of these nitronic structures are cleanly eliminated by the PMR spectrum of the adduct.

either refluxing a solution of VI or by heating VI as a melt at 140°. This material could also be isolated from the residues of the reaction of I and II. The elemental analysis of IX indicated that it was formed from VI by the loss of a molecule of ethanol. The IR spectrum of IX indicated the retention of an olefinic linkage (1600 cm^{-1}). Two carbonyl absorptions (1701 and 1795 cm^{-1}) were observed corresponding to ester and five-membered lactone carbonyls respectively; no amide bands were observed in the spectrum. The UV spectrum of IX (λ_{max} = 211, 311 mμ) was quite similar to that of VI; the amide VIII would be expected to show a typical acetanilido absorption (λ_{max} = ca. 240 mμ).[15]

On the basis of this data, formulation VIII could be ruled out as the structure of the thermal transformation product. The cyclic structure, 2-phenyl-3-carbethoxy-5-isoxazolone (IX), is consistent with all the data cited above; it could be formed readily from VI by a simple intramolecular transesterification process. This structural assignment was further supported by a comparison of IX with its known N-methyl analog (X).[16] The IR spectra of IX and X are almost identical; in analogy to the behavior of X,[16] IX underwent basic hydrolysis to give the monoanilide of malonic acid.



IX

The postulated structure of IX was confirmed by its PMR spectrum, which showed the following four groups of resonances similar to those observed in the spectrum of VI. (a) A one-proton singlet at $\tau = 1{\cdot}08$ for the olefinic proton. The extra deshielding of this proton relative to that of the analogous proton of VI ($\tau = 1{\cdot}68$) is probably due largely to the different spatial orientation of the lactone carbonyl group in IX. In this structure, the olefinic proton is now fixed in a position in the plane of and "behind" the lactone carbonyl group, circumstances well-known to result in marked extra deshielding. (b) A five-proton complex from the aromatic hydrogens centered at $\tau = 2{\cdot}53$, similar to that observed for VI, but again at slightly lower fields. (c) A two-proton quartet ($\tau = 5{\cdot}68$) and a three proton triplet ($\tau = 8{\cdot}67$), J_{HH} = ca. 7·2 c/s, indicating the presence of only one ethoxyl group as required by structure IX.

1,1-*Diphenylethylene and nitrosobenzene*

The reaction of I and III in chloroform at ambient temperatures gave a product (V or VII) with the reported physical properties.[5,6] Elementary analytical data was consistent with both structures, but did not serve to distinguish between the two possibilities since they differ by only a methylene group. The product absorbed at 232 and 208 mμ in the UV; again, only anilino absorption (ca. 240 mμ) would be expected for V. The observed UV absorption is consistent with structure VII; the

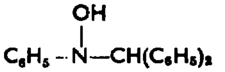
---

[15] A. P. DeJonge and W. Den Hertog, *Rec. Trav. Chim.* **75**, 4 (1956).

[16] H. Ulrich, J. N. Tilley and A. A. Sayigh, *J. Org. Chem.* **27**, 2160 (1962).

model compound, α,N-diphenylnitrone (XI) is reported to absorb at 232 and 314 mμ.[17] The limited solubility of the product precluded any extensive study of its PMR spectrum, but a spectrum was obtained at 75° in DMF-d_7 solution and only aromatic proton absorptions were observed.

Final proof of the structure of this product rested on a direct synthetic approach. Reduction with LAH gave a hydroxylamine (XII) which was identical in all respects with the product formed by the addition of phenylmagnesium bromide to XI. Oxidation of XII with hydrogen peroxide, I or cupric acetate gave VII. Thus the



$C_6H_5-N(OH)-CH(C_6H_5)_2$

XII

structure proposed by Lapworth is confirmed and the reaction of I and III follows the general behavior established by the studies of Alessandri.[7,18]

In the studies carried out by Alessandri,[7] no indication was obtained of the fate of the terminal carbon which is cleaved during the course of formation of nitrones from vinylbenzenes. In the present study, no evidence for the formation of either carbon dioxide or formaldehyde could be obtained from the reaction of I and III in the absence of solvent at 80°. Chromatography of the reaction residues after the isolation of VII showed only the presence of azoxybenzene, benzophenone and unreacted III; no evidence for a one carbon fragment was obtained. Distillation of reaction residues gave III, benzophenone and N,N′-diphenylurea. The latter material had been isolated by Ingold[5] by a similar treatment and was postulated to arise by oxidation of a C_6H_5NC fragment of phenylisocyanate which is known to form the urea in the presence of trace amounts of moisture. The demonstrated absence of the urea prior to distillation indicates it to be an artifact of the distillation and not a primary reaction product. Thus, no information bearing on the fate of the cleaved carbon was obtained from these studies.[19]

With the refutation of the oxazetidine formulations for these products, the fluorinated compounds[3] and the tetramethoxy compound[4] remain the only authentic examples of this ring system.[20]

---

[17] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.* **22**, 576 (1957).

[18] Two additional structures were considered for the reaction product of I and III. The absence of hydroxyl and olefinic absorptions in the IR eliminated the possibility of a vinylhydroxylamine analogous to VI. The possibility of a nitronic structure, $C_6H_5N(O){=}CHCH(C_6H_5)_2$ (i) was eliminated by comparison with an authentic sample of i prepared by the reaction of β,β-diphenylacetaldehyde and N-phenylhydroxylamine. Additionally, the PMR spectrum of the product was inconsistent with both of the alternative structures.

[19] In studies[9b] of the corresponding reaction of I with styrene which leads to the formation of α,N-diphenylnitrone, tetrahydro-1,2,5-oxadiazole-N-oxides have been shown to be the initial reaction products. Thermal collapse of these intermediates leads to the nitrone. The carbon cleaved in this process appears as formanilide. It is probable that the reaction of I and III follows the same course. No evidence was obtained for the formation of oxadiazoles in this study, but it must be noted that the intermediates isolated in the styrene study were highly unstable and were only obtained by low temperature column chromatography.

[20] Recent studies of the adduct of hexachlorocyclopentadiene and I indicate a perchlorocyclopentano-oxazetidine ring structure: C. E. Griffin and N. F. Hepfinger, unpublished observations.

EXPERIMENTAL[21]

N-*Phenyl*-N-*(β,β-dicarbethoxyvinyl)hydroxylamine* (VI)

A solution of 1·07 g (0·01 mole) nitrosobenzene in 10 ml dry $CHCl_3$ was added dropwise to a colorless refluxing solution of 2·48 g (0·015 mole) diethyl methylenemalonate[22] in 20 ml $CHCl_3$. The addition rate was adjusted to allow complete decoloration of each drop of the green nitrosobenzene solution. Complete addition (ca. 45 min) afforded a clear yellow solution. Evaporation of the solvent under red. press. at ambient temp gave a bright yellow semi-solid which was crystallized by trituration with 2 ml ether. The pale yellow crystalline solid (1·37 g, 49%) was collected, recrystallized 3 times from dry ether and dried over P_2O_5 to give colorless needles of VI, m.p. 96·0–96·5° (lit. m.p., 98–100°,[5] 98–99°).[6] Found: C, 60·45; H, 5·99; N, 5·14. Calc. for $C_{14}H_{17}O_5N$: C, 60·22; H, 6·09; N, 5·07%.)

The IR spectrum of VI showed absorptions at 3521 w, 1701 s, 1639 s, 1600 m, 1558 s, 1439 s, 1449 w, 1412 s, 1383 s, 1351 s, 1290 m and 1081 s cm^{-1}. The UV absorption of VI showed λ_{max} = 222, 317 mμ (ε = 10,900, 32,700) and λ_{min} = 258 mμ (ε = 2,100).

The hydroxylamine (VI) was readily oxidized by $KMnO_4$ in acetone solution. The hydroxylamine was identical in all respects with an authentic sample prepared from N-phenylhydroxylamine and diethyl hydroxymethylenemalonate.[6]

2-*Phenyl-4-carbethoxy-5-isoxazolone* (IX)

Addition of 14·0 g (0·081 mole) diethyl methylenemalonate to a solution of 14·0 g (0·013 mole) nitrosobenzene in 8 ml $CHCl_3$ resulted in a vigorous exothermic reaction which caused refluxing of the solvent. After the reaction subsided, the reaction mixture was allowed to cool to room temp and the solvent was removed under red. press. to give a brown semi-solid. Trituration of this solid with 5 ml ether gave a pale yellow solid (6·0 g, 27%), m.p. 99–100°, which was identified as VI. The ethereal solution was reduced in volume; dropwise addition of pentane gave a crystalline precipitate which was collected in fractions until the deposition of solid material ceased. The m.ps of the material obtained from successive fractions rose to a final value of 130°. Recrystallization of the final fraction from a 1:1 acetone–cyclohexane mixture gave colorless needles of IX which, after drying over P_2O_5, melted at 131–132°. (Found: C, 61·90; H, 4·93; N, 6·11. Calc. for $C_{12}H_{11}O_4N$: C, 61·79; H, 4·76; N, 6·01%.)

The IR spectrum of IX showed absorptions at 1795 s, 1701 s, 1603 m, 1576 s, 1560 m, 1479 w, 1447 w, 1393 w, 1357 m, 1348 m, 1325 w, 1299 w, 1140 s, 1094 w, 1068 w, 957 w and 905 w cm^{-1}. The UV absorption of IX showed λ_{max} = 211, 311 mμ (ε = 21,600, 35,500) and λ_{min} = 260 mμ (ε = 4,000).

Recrystallization of the intermediate pentane precipitated fractions from acetone–cyclohexane mixtures gave additional quantities of IX.

It was subsequently found that VI could be converted to IX in 60–90% yields by the following thermal treatments: (a) refluxing a solution of VI in dioxane, cyclohexane or other higher boiling solvents for 2 hr; (b) heating a melt of VI to 140° until the evolution of gas (EtOH) ceased; (c) brief exposure of a melt of VI to temp in excess of 180°.

Chromatographic separation of the residual yellow oils obtained from these reactions afforded trace amounts of azoxybenzene which was identified by comparison with an authentic sample. Azoxybenzene was eluted from alumina columns with ether.

---

[21] All m.ps are uncorrected. IR spectra were recorded with either a Perkin–Elmer Model 21 or a Beckman IR-8 spectrophotometer using dilute solutions ($CHCl_3$) in 0·1 mm NaCl cells. UV spectra were recorded with a Cary Model 14 spectrophotometer using 95% ethanolic solutions. All PMR spectra were obtained with a Varian Associates A-60 spectrometer; sample temp 37 ± 1°. Dilute solutions in $CDCl_3$ were employed; chemical shifts are reported on the τ-scale and are precise to ±0·008 ppm or better. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

[22] Prepared according to the procedure of W. Feeley and V. Boekelheide, *Organic Syntheses* **38**, 22 (1958). Because of the polymerization of the monomer, the purity of the starting material was not specifically determined. However, the yield of VI in this reaction never exceeded 53% even with repeatedly distilled samples of the malonate.

Basic hydrolysis of 2-phenyl-4-carbethoxy-5-isoxazolone (IX)

The isoxazolone IX (0·05 g, 0·0021 mole) was shaken with 10% NaOH aq for 15 min. The reaction mixture was acidified with 10% HCl aq and extracted with two 50 ml portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered and the solvent was removed under vacuum to give 0·3 g (77%) of malonic acid monoanilide, melting with evolution of gas at 127–130°. Recrystallization from aqueous ethanol or water gave colorless crystals, m.p. (dec) 132° (lit.[23] dec 132°).

The monoanilide decomposed at its m.p. with loss of CO_2 (detected with $Ba(OH)_2$ aq) to give a quantitative yield of acetanilide, identified by comparison with an authentic sample.

α,α,N-*Triphenylnitrone* (VII)

1,1-Diphenylethylene (33·6 g, 0·187 mole) was added in one portion to a solution of 20 g (0·187 mole) nitrosobenzene in 30 ml $CHCl_3$. The homogeneous reaction mixture was stirred for 18 hr, changing from grass green to reddish brown. Evaporation of the solvent under red. press. gave a dark brown residue: the residue was slurried with 50 ml of ether to give 5·9 g (12%) of impure VII, m.p. 218–223° after air drying. Three recrystallizations from 95% EtOH and drying over P_2O_5 gave a constant m.p. of 229–230°. (Found: C, 83·53; H, 6·01; N, 5·14. Calc. for $C_{19}H_{15}NO$ (VII): C, 83·60; H, 5·60; N, 5·16. Calc. for $C_{20}H_{17}NO$ (1:1 adduct, V): C, 83·62; H, 5·92; N, 4·90%.)

The IR spectrum of VII showed absorptions at 1965 w, 1844 w, 1764 w, 1595 w, 1495 m, 1447 s, 1351 m, 1159 w, 1098 s, 1073 s, 1002 w and 959 s cm^{-1}. The UV spectrum of VII showed $\lambda_{max} = 232$, 308 mμ ($\varepsilon = 13{,}800$, 10,300), $\lambda_{infl} = 248$ mμ and $\lambda_{min} = 218$, 268 mμ ($\varepsilon = 12{,}600$, 5,100).

After the isolation of VII, the ethereal solutions were evaporated to a dark oil under red. press. and subjected to crude fractionation at 0·5 mm to give: (A) forerun to 105°, a green oil which was shown to be a mixture of starting materials, predominately the olefin; (B), b.p. 105–110°, a pale yellow oil identified as the olefin; (C) b.p. 110–144°, an orange oil (4·2 g) which partially crystallized; (D) b.p. 144–155°, 2·0 g of an orange oil.[24]

The solid from fraction C was removed by filtration, washed with ether and recrystallized from EtOH to give colorless crystals of N,N-diphenylurea, m.p. 248°; the identity of the urea was established by comparisons with an authentic sample. Treatment of fraction D with an alcoholic solution of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 240–241°, identified by comparison with an authentic sample.

Simple 1:1 molar ratios of the reactants in the absence of solvent underwent a mild exothermic reaction at room temp; heating these mixtures to 80° resulted in a highly exothermic reaction. No evolution of gas (CO_2 or formaldehyde) could be detected in these reactions. Several attempted reactions involving slow addition of nitrosobenzene to the olefin in refluxing $CHCl_3$ were unsuccessful; decoloration of the nitrosobenzene solution could not be effected even with extremely slow rates of addition and extended periods of reflux lead to decomposition and tar formation.

In a repetition of the reaction, a solution of 4·5 g (0·042 mole) nitrosobenzene and 5·0 g (0·028 mole) 1,1-diphenylethylene in 20 ml $CHCl_3$ was allowed to stand at room temp for 24 hr. The solvent was removed under red. press. at room temp to give a brown oily residue which was held at a press. of 1·0 mm until the sublimation of unreacted nitrosobenzene (0·41 g) ceased. The residual brown tar was dissolved in 100 ml dry ether and cooled to 0° to yield 1·7 g (21%) VII. The ethereal filtrate was reduced in volume and extracted with two 50 ml portions of pet. ether (b.p. 30–65°) leaving 0·8 g tar which was discarded. The extract which contained 7·0 g of material was chromatographed on a 150 g alumina column (2·5 cm diameter) to yield 2·90 g 1,1-diphenylethylene; 2·25 g of a yellow oil, largely azoxybenzene; 0·78 g benzophenone and 0·35 g unidentified colored oils.

N-*Benzhydryl*-N-*phenylhydroxylamine* (XII)

A. *By reduction of* α,α,N-*triphenylnitrone* (VII). A slurry of 2·0 g (0·075 mole) of VII in 30 ml absolute ether was added dropwise to a stirred ethereal slurry of LAH (0·8 g, 0·21 mole) during a period of 1 hr. After the vigorous reaction had subsided, the mixture was refluxed for an additional hr. Excess hydride was decomposed with ethyl acetate and the reaction mixture was poured into an

---

[23] F. Chattaway and J. Olmstead, *J. Chem. Soc.* **97**, 939 (1910).

[24] The orange color of fractions C and D is presumably due to the co-distillation of azobenzene which could arise from the thermal decomposition of azoxybenzene. The presence of the latter material has been demonstrated in the reaction mixtures.

excess of 10% H_2SO_4 aq. The ether layer was separated and the aqueous acid layer was extracted twice with 20 ml portions of ether. The combined ethereal solutions were dried over $MgSO_4$, filtered and concentrated under red. press. to give a yellow oil (1·8 g). Addition of water to a methanolic solution of the yellow oil gave a colorless precipitate of XII, 1·5 g (75%). After drying over P_2O_5, XII melted at 129–130°. (Found: C, 83·32; H, 6·46; N, 4·91. Calc. for $C_{19}H_{17}NO$: C, 83·03; H, 6·25; N, 5·01%.)

The IR spectrum of XII showed absorptions at 3571 m, 3333 w, 1957 w, 1875 w, 1804 w, 1755 w, 1603 s, 1495 s, 1453 s, 1346 m, 1299 m(sh), 1176 w, 1155 w, 1108 w, 1075 m, 1000 w, 1056 w and 865 w cm^{-1}.

B. *By addition of phenylmagnesium bromide to* α,N-*diphenylnitrone*. An ethereal solution of PhMgBr prepared from 3·16 g (0·02 mole) bromobenzene and 0·61 g (0·025 mole) Mg in 35 ml dry ether was treated with a solution of 3·94 g (0·02 mole) α,N-diphenylnitrone[25] in 50 ml ether. After the addition was completed, the reaction mixture was slurried with ice and 5% H_2SO_4 aq was added to dissolve the precipitated salts. The ether layer and three additional 50 ml ether extracts were combined, dried over $MgSO_4$ filtered and reduced in volume under red. press. Addition of water to a cold ethanolic solution of the residual oil gave a precipitate. Recrystallization of the precipitate as in the preceding experiment gave 3·6 g (65%) XII, m.p. 128–129°. The material was identical in all respects with that prepared by reduction of VII.

Oxidation of N-*benzhydryl*-N-*phenylhydroxylamine* (XII)

Nitrosobenzene (2·14 g, 0·02 mole) was added in one portion to a cooled solution of XII dissolved in a minimal amount of $CHCl_3$. The ensuing moderately exothermic reaction was complete in 15 min; 50 ml ether were added and the insoluble residues were collected. Three recrystallizations from EtOH gave 2·05 g (75%) VII, m.p. 229–230°, identified by comparison with a sample prepared by the reaction of I and III. Oxidations with hydrogen peroxide[26] and cupric acetate gave similar results.

---

[25] E. Bamberger, *Ber. Dtsch. Chem. bes.* **27**, 1556 (1894).

[26] G. E. Utzinger, *Liebigs Ann.* **556**, 50 (1944); J. Thesing and H. Mayer, *Chem. Ber.* **89**, 2159 (1956).