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REINVESTIGATION OF CYCLOADDITION OF NITROSOBENZENE TOWARDS 1,3-DIPHENYLISOBENZOFURANS

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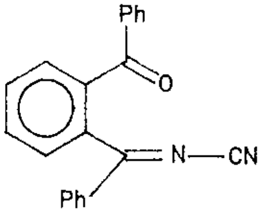
Abstract — The title reaction gives rearrangement product of N-phenyl-α-phenyl-α-(o-benzoylphenyl)nitrones (8) rather than the earlier reported Diels-Alder cycloadduct 2. The molecular structure of **8a** has been confirmed by a single crystal X-ray diffraction study.

Nitrosobenzene is one of the carbon-nitroso compounds known to be a reactive heterodienophile in the Diels-Alder reaction.[2] Extensive studies of cycloaddition reveal that nitrosobenzene reacts regioselectively towards unsymmetrical dienes.[3] Earlier, Mustafa reported that nitrosobenzene cyclized with 1,3-diphenylisobenzofuran (**1a**) to afford the corresponding Diels-Alder cycloadduct **2a**.[4] Several years ago, Kirby and his co-workers found that nitrosyl cyanate reacted with 1,3-diphenylisobenzofuran in a different manner. The major products were 1,2-dibenzoylbenzene and N-cyanoimine **3** in a ratio of 1 : 1.[5] The outcome of the reaction was rationalized by oxygen atom transfer from the transient intermediate, N-cyanonitrone **4** or N-cyanoxaziridine **5**, to the reactant, 1,3-diphenylisobenzofuran and/or by the recombination of unreacted reactant with cyanonitrene, a fragment cleavaged from the unstable Diels-Alder cycloadduct **6**.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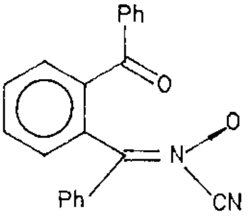
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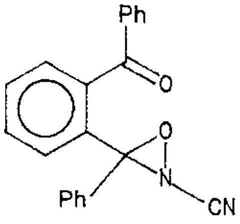
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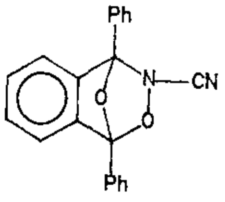

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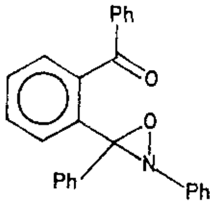

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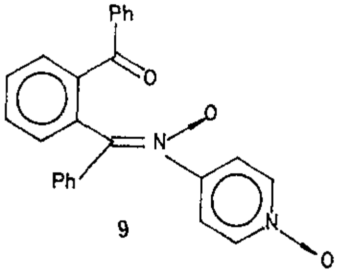

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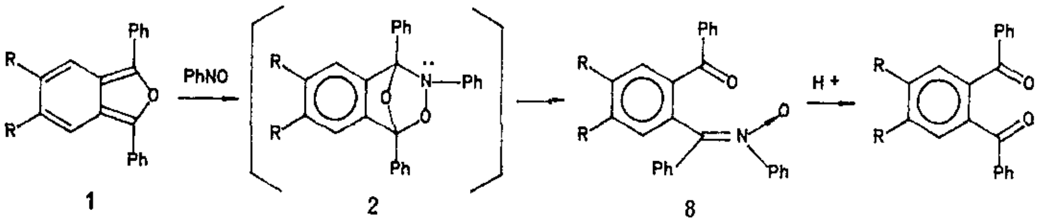
In connection with our studies on the Diels-Alder reaction of trichloronitrosomethane,[6] we undertook the reinvestigation of the reaction of nitrosobenzene with 1,3-diphenylisobenzofurans. In this paper, we wish to describe the results that are different with the ones reported earlier by Mustafa [4] and Kirby [5].



a R = H

b R = CH_3

Treatment of nitrosobenzene with **1a** in ethyl alcohol as reported[4] afforded a stable light yellow crystal in the yield of 64%. Its melting point, microanalysis and molecular ion of the mass spectrum were found to be identical with the data reported for cycloadduct **2**.[4] However, the ir spectrum shows a strong absorption band at 1665 cm^{-1} which can only be accounted by a conjugated C=O stretching. The presence of carbonyl group is further established by the signal at 194.0 ppm in its ^{13}C-nmr spectrum. Apparently, the structure of product was assigned incorrectively by earlier investigator.[4] Due to the absence of critical evidence for distinguishing between two possible structures **7** and **8a**, an X-ray structure analysis was taken. The crystal structure[7] reveals a notable C-N-O angle of 124.1° and an N-C(14) length of 1.311 Å (Tables 1 and 2) which should exclude the consideration of N-phenyloxaziridine **7** and unambiguously established the structure of product as nitrone **8a**.[8] A view of molecule **8a** is given in Figure 1.

Under the similar conditions, the reaction of nitrosobenzene with 5,6-dimethyl-1,3-diphenylisobenzofuran (1b) exhibited similar results to afford **8b**.[9] Attempts of isolation of the preliminary cycloadduct 2 by decreasing the reaction temperature to -78 °C were unsuccessful. Neither the reaction

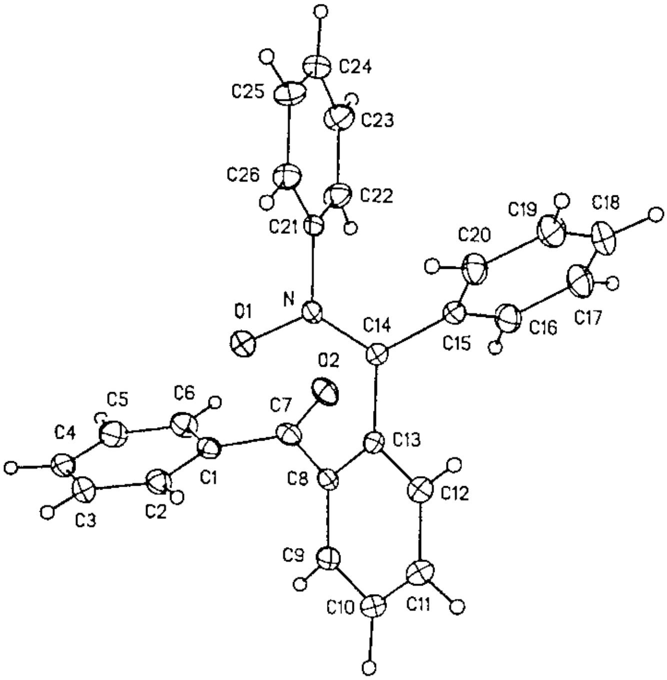


Fig. 1 ORTEP diagram of the X-ray crystal structure of nitrone **8a**

Table 1. Bond angles data for nitrone **8a**

O(1)-N-C(14)	124.1(3)	O(1)-N-C(21)	114.4(3)
C(14)-N-C(21)	121.3(3)	C(2)-C(1)-C(6)	118.5(4)
C(2)-C(1)-C(7)	122.5(4)	C(6)-C(1)-C(7)	119.0(4)
C(1)-C(2)-C(3)	120.7(5)	C(2)-C(3)-C(4)	120.1(5)
C(3)-C(4)-C(5)	120.1(5)	C(4)-C(5)-C(6)	120.0(5)
C(1)-C(6)-C(5)	120.6(5)	O(2)-C(7)-C(1)	121.1(4)
O(2)-C(7)-C(8)	119.0(3)	C(1)-C(7)-C(8)	119.8(3)
C(7)-C(8)-C(9)	119.6(4)	C(7)-C(8)-C(13)	120.7(3)
C(9)-C(8)-C(13)	119.3(4)	C(8)-C(9)-C(10)	121.2(4)
C(9)-C(10)-C(11)	120.0(5)	C(10)-C(11)-C(12)	119.7(5)
C(11)-C(12)-C(13)	121.4(4)	C(8)-C(13)-C(12)	118.4(4)
C(8)-C(13)-C(14)	123.3(3)	C(12)-C(13)-C(14)	118.2(3)
N-C(14)-C(13)	119.6(3)	N-C(14)-C(15)	120.6(3)
C(13)-C(14)-C(15)	119.8(3)	C(14)-C(15)-C(16)	119.7(4)
C(14)-C(15)-C(20)	120.8(3)	C(16)-C(15)-C(20)	119.4(4)
C(15)-C(16)-C(17)	120.1(4)	C(16)-C(17)-C(18)	120.3(5)
C(17)-C(18)-C(19)	119.8(5)	C(18)-C(19)-C(20)	121.4(5)
C(15)-C(20)-C(19)	119.0(4)	N-C(21)-C(22)	118.7(3)
N-C(21)-C(26)	119.5(3)	C(22)-C(21)-C(26)	121.8(4)
C(21)-C(22)-C(23)	118.7(4)	C(22)-C(23)-C(24)	119.9(4)
C(23)-C(24)-C(25)	121.0(5)	C(24)-C(25)-C(26)	120.0(4)
C(21)-C(26)-C(25)	118.3(4)		

temperature (-78 °C to 80 °C) nor solvents (methylene chloride, ether and benzene) have influence on the formation and the yield of nitrone 8.

Table 2. Bond lengths data (Å) for nitrone **8a**

O(1)-N	1.299 (4)	O(2)-C(7)	1.218 (5)
N-C(14)	1.311 (5)	N-C(21)	1.452 (5)
C(1)-C(2)	1.389 (6)	C(1)-C(6)	1.380 (7)
C(1)-C(7)	1.494 (5)	C(2)-C(3)	1.382 (6)
C(3)-C(4)	1.371 (8)	C(4)-C(5)	1.370 (8)
C(5)-C(6)	1.390 (7)	C(7)-C(8)	1.497 (6)
C(8)-C(9)	1.383 (6)	C(8)-C(13)	1.402 (5)
C(9)-C(10)	1.382 (7)	C(10)-C(11)	1.370 (7)
C(11)-C(12)	1.380 (7)	C(12)-C(13)	1.395 (6)
C(13)-C(14)	1.481 (5)	C(14)-C(15)	1.484 (5)
C(15)-C(16)	1.378 (6)	C(15)-C(20)	1.381 (6)
C(16)-C(17)	1.385 (7)	C(17)-C(18)	1.359 (8)
C(18)-C(19)	1.356 (8)	C(19)-C(20)	1.386 (7)
C(21)-C(22)	1.377 (6)	C(21)-C(26)	1.368 (6)
C(22)-C(23)	1.381 (7)	C(23)-C(24)	1.363 (7)
C(24)-C(25)	1.363 (7)	C(25)-C(26)	1.388 (6)

4-Nitrosopyridine-N-oxide, known for its "ene" reaction with tetramethylethylene[10] has not hitherto been employed as a dienophile. When 1,3-diphenylisobenzofuran was treated with 4-nitrosopyridine-N-oxide at 0 °C, the desired product 9 was isolated in the yield of 38 %. The structure of nitrone 9 was determined on the basis of spectroscopic analysis and high resolution mass spectrum.[11]

Attention was then turned to the examination of oxygen atom transfer between nitrone 8 and isobenzofurans as suggested by the mechanism proposed by Kirby et al. for the reaction of nitrosyl cyanate with **1**.[5] Thus, refluxing the mixture of 1,3-diphenylisobenzofuran and nitrone **8a** in benzene or toluene under oxygen-free nitrogen atmosphere for 24 hours did not give any products. All the reactants were chromatographically recovered. The nitrones 8 and 9 are relatively stable in the air for weeks, however, hydrolysis of **8a** in aqueous acid solution produced 1,2-dibenzoylbenzene in quantitatively yield.

ACKNOWLEDGEMENT

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6. a) C. T. Lin and J. H. Chen, J. Chin. Chem. Soc., 1987, **34**, 317; b) We have found that trichloronitrosomethane reacted with 1,3-diphenylisobenzofurans to produce 1,2-dibenzoylbenzenes in high yield. The corresponding Diels-Alder cycloadducts were unable to be isolated. See also ref.1.
7. Crystallographic data for $C_{26}H_{19}NO_2$ (**8a**): orthorhombic, space group Pbca (No.61), a = 11.264(4) Å, b = 16.418(3) Å, c = 21.771(6) Å, V = 4026(2) $Å^3$, Z = 8, FW = 377.4, D_c = 1.245 g/cm^3, λ = 0.71073 Å. Of the 3414 reflections measured at room temperature on a Nicolet R3m/V diffractometer, 3023 were unique and 1470 reflections were considered observed ($I > 3\sigma(I)$) after LP corrections. The structure was solved by direct methods and refined by full matrix least-squares refinement. R = 0.042, R_w = 0.043, GOF = 1.42. Highest peak on final difference map = 0.37 e/A^3. All calculations were performed on a Micro VAX II based Nicolet SHELXTL PLUS system.
8. **8a** (64 % yield): mp 227 °C (lit.[4] 230 °C), ^{1}H-nmr ($CDCl_3$) δ 8.01 (d, 1 H, J = 8.1 Hz), 7.93 (d, 1 H, J = 8.4 Hz), 7.41 (m, 6 H), 7.19 (m, 11 H); ^{13}C-nmr ($CDCl_3$) δ 194.0 (s), 147.0 (s), 146.7 (s), 139.8 (s), 136.2 (s), 135.2 (s), 134.5 (s), 132.4 (d), 131.3 (d), 130.7 (d), 130.6 (d), 130.3 (d), 128.8 (d), 128.7 (d), 128.6 (d, two peaks), 128.4 (d), 128.1 (d, two peaks), 124.3 (d); ir (KBr) 3030, 1665 cm^{-1}; ms (12 ev) m/z 377 (M^+), 361 (M^+-16), 270 (M^+- C_6H_5NO, base peak); Anal. Calcd for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71; Found: C, 82.80; H, 5.02; N,3.73
9. **8b** (89 %): mp 189 °C; ^{1}H-nmr ($CDCl_3$) δ 7.98 (d, 1 H, J = 7.2 Hz), 7.90 (d, 1 H, J = 7.7 Hz), 7.46 (m, 3 H), 7.15 (m, 11 H), 6.95 (s, 1 H), 2.25 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3); ^{13}C-nmr ($CDCl_3$) δ 194.2 (s), 147.6 (s), 147.1 (s), 139.2 (s), 137.2 (s), 136.6 (s), 135.2 (s), 132.1 (d), 132.1 (s), 132.0

(d), 130.5 (d), 130.4 (d), 130.0 (d), 129.9 (s), 128.5 (d), 128.4 (d), 128.3 (d), 127.9 (d), 127.8 (d), 124.2 (d), 19.62 (q), 19.58 (q); ir (KBr) 3030, 1665 cm^{-1}; ms (12 ev) m/z 405 (M^+), 389 (M^+-16), 298 ($M^+-C_6H_5NO$, base peak); Anal. Calcd for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45; Found: C, 82.96; H, 5.76; N, 3.32

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11. 9 (38 %): mp 198 °C; ^{1}H-nmr ($CDCl_3$) δ 8.05-7.85 (m, 4 H), 7.15-7.70 (m, 14 H); ^{13}C-nmr ($CDCl_3$) δ 194.2 (s), 149.5 (s), 143.5 (s), 139.6 (d), 139.4 (s), 135.7 (s), 134.1 (s), 133.6 (s), 132.7 (d), 131.3 (d), 130.7 (d), 130.5 (d), 130.4 (d), 129.9 (d), 129.3 (d), 128.8 (d), 128.7 (d), 128.2 (d), 122.2 (d); ir (KBr) 3035, 1660 cm^{-1}; HRMS for $C_{25}H_{18}N_2O_3$ Calcd : 394.1317; Found: 384.1321

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