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The Wolff Rearrangement and 1,3-Dipolar Cycloaddition of 2-Diazo-3,4-bis(diphenylmethylene)cyclobutanone[1)]

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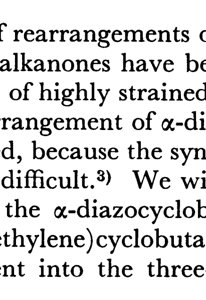
The first example of the Wolff rearrangement of α-diazocyclobutanone, the title diazo ketone (**2**), into the three-membered cyclic ketene (**4**) was observed. The ketene intermediate (**4**) could be trapped by its reaction with alcohols, aniline, azobenzene, and *N*-benzylideneaniline to afford 1-alkoxycarbonyl- (**5a**—**c**) and 1-phenylcarbamoyl-2,3-bis(diphenylmethylene)cyclopropane (**5e**), and 1,2-bis(diphenylmethylene)-5,6-diphenyl-5,6-diaza- (**9**) and 1,2-bis(diphenylmethylene)-5,6-diphenyl-5-azaspiro[2,3]hexan-4-one (**10a**), respectively. In contrast to the rearrangement, **2** directly reacted with *p*-benzoquinone and nitrosobenzene, affording the corresponding 1,3-dipolar cycloadducts (**14** and **15**).

The Wolff rearrangements of six- and five-membered α-diazocycloalkanones have been extensively applied to the synthesis of highly strained compounds.[2)] However, no such rearrangement of α-diazocyclobutanone has yet been reported, because the synthesis of the α-diazocyclobutanone is difficult.[3)] We wish now to report the first synthesis of the α-diazocyclobutanone, 2-diazo-3,4-bis(diphenylmethylene)cyclobutanone (**2**), and its Wolf rearrangement into the three-membered cyclic ketene (**4**).



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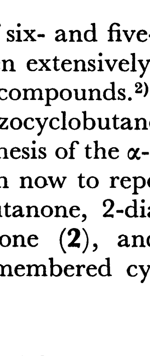

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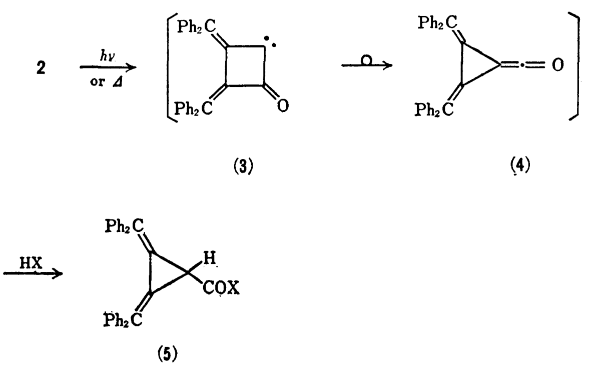
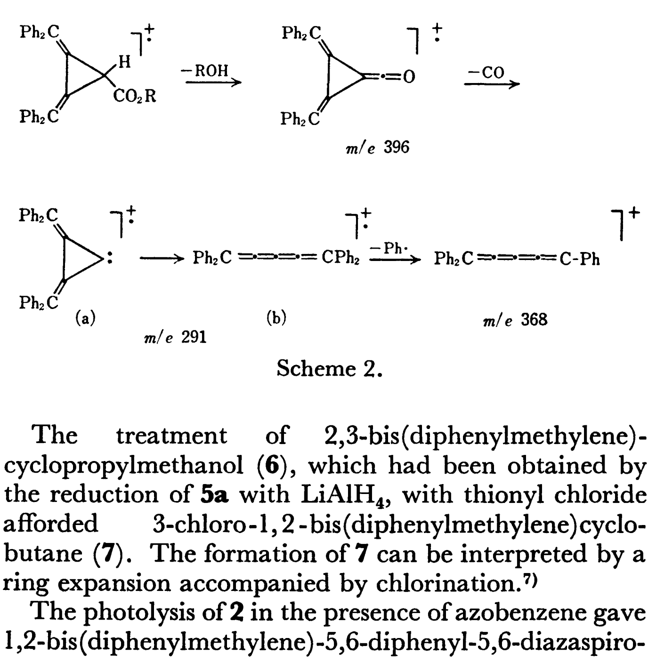
Diazo ketone (**2**) was prepared by the treatment of 3,4-bis(diphenylmethylene)cyclobutanedione tosylhydrazone (**1**), which had been derived from 3,4-bis(diphenylmethylene)cyclobutanedione[4)] and tosylhydrazine, with basic aluminum oxide; the overall yield was 95%. The irradiation of **2** in the presence of water, ROH, and an aniline afforded 1-carboxy-(**5d**), 1-alkoxycarbonyl-(**5a**—**c**), and 1-phenylcarbamoyl-2,3-bis(diphenylmethylene)cyclopropane (**5e**) respectively in the yields summarized in Table 1. Although the photolysis of **2** in the presence of water afforded **5d** in a very low yield, the thermal decomposition of **2** in aqueous dioxane afforded **5d** in a relatively high yield (52%). The above trapping reactions support the intermediacy of **4** in both the photolysis and thermolysis of **2**.



Scheme 1.

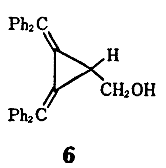
The structures of all the rearrangement products (**5a**—**e**) were elucidated on the basis of their spectral data (Table 1). In the mass spectra, all the esters (**5a**—**c**) showed a fragment ion ($C_{23}H_{15}^+$, *m/e* 291) as the base peak; a reasonable fragment pattern of **5** is as follows: The rearrangement of the cation radical (**a**) into **b** is similar to the cyclopropylidene-allene rearrangement.[5)] In the UV spectra, the absorption bands of **5a**—**e** (λ_{max} 370—374 nm) appeared at a longer wavelength region than that of **8**[6)] (λ_{max} 357 nm). This bathochromic shift is probably due to a ring strain of **5**.



Scheme 2.

The treatment of 2,3-bis(diphenylmethylene)cyclopropylmethanol (**6**), which had been obtained by the reduction of **5a** with LiAlH₄, with thionyl chloride afforded 3-chloro-1,2-bis(diphenylmethylene)cyclobutane (**7**). The formation of **7** can be interpreted by a ring expansion accompanied by chlorination.[7)]

The photolysis of **2** in the presence of azobenzene gave 1,2-bis(diphenylmethylene)-5,6-diphenyl-5,6-diazaspiro[2.3]hexan-4-one (**9**) in a 75% yield. The photolysis and thermolysis of **2** in the presence of benzylideneaniline and *N*-(diphenylmethylene)aniline afforded 5,6-



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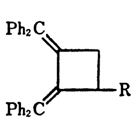


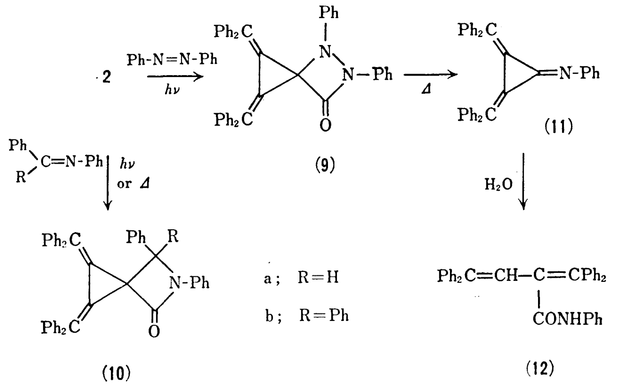
7 R=Cl
8 R=H

Table 1. Physical properties, yields, analytical data of **5a–e**

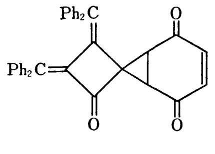
Compd	X	Yield (%)	Mp (°C)	$\nu_{C=O}^{KBr}$ (cm^{-1})	$\lambda_{max}^{CHCl_3}$ nm ($\varepsilon\times10^{-2}$)	τ_{C-H}[b]	Found (Calcd) (%) C	H
5a	OMe	87	157—159	1725	262 (282)	6.72	86.67	5.40
					373 (360)		(86.89	5.65)
5b	OEt	65	128—129	1720	264 (298)	6.70	86.62	5.87
					374 (376)		(86.85	5.92)
5c	O*i*-Pr	75	161—162	1710	260 (297)	6.75	86.64	6.12
					370 (360)		(86.81	6.18)
5d	OH	13	217—218	1695	263 (259)	6.75	86.70	5.07
		(52)[a]			373 (360)		(86.93	5.35)
5e	NHPh	45	171—172	1645	254 (332)	6.63	88.14	5.52
					373 (339)		(88.31	5.56)

a) Yield obtained by thermolysis in aq dioxane. b) Chemical shift of the ring proton.

diphenyl- (**10a**) and 5,6,6-triphenyl-1,2-bis(diphenylmethylene)-5-azaspiro[2.3]hexan-4-one (**10b**) respectively. These reactions can be interpreted in terms of the cycloaddition of the ketene (**4**) with azobenzene and imines, because it has been known that the reaction of ketene with N=N or C=N bonds affords the corresponding cycloaddition product.[8] The thermolysis of diazetidinone (**9**) easily afforded 1,2-bis(diphenylmethylene)-3-phenyliminocyclopropane (**11**) quantitatively; on hydrolysis, this afforded 1,1,4,4-tetraphenyl-2-phenylcarbamoyl-1,3-butadiene (**12**, 75%).



Scheme 3



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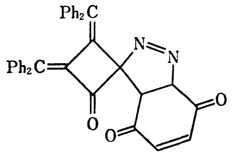

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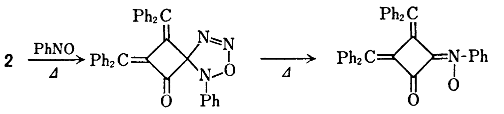
On the contrary, the photolysis and thermolysis of **2** in the presence of *p*-benzoquinone afforded 2,3-bis(diphenylmethylene)-4,4-(3,6-dioxo-4-cyclohexen-1,2-ylene)cyclobutanone (**13**) in 45 and 59% yields respectively. However, when a mixture of **2** and *p*-benzoquinone in benzene was kept at room temperature, 5,6-diaza-7,8-(1,4-dioxo-2-butylene)-2,3-bis(diphenylmethylene)spiro[3,4]octan-1-one (**14**) was obtained in an 80% yield. The heating of **14** easily afforded **13** quantitatively. Finally, it is clear that the conversion of **2** into **13** proceeds *via* **14**. Similarly, the reaction of **2** with nitrosobenzene afforded 2,3-bis(diphenylmethylene)-8-phenyl-5,6,8-triaza-7-oxaspiro[3.4]oct-5-en-1-one (**15**) and 2,3-bis(diphenylmethylene)-4-phenyliminocyclobutan-1-one *N*-oxide (**16**) in 15 and 50% yields respectively. The 1,3-dipolar cycloadduct (**15**) was thermally unstable and was easily converted into **16** at room temperature. To our best knowledge, no such 1,3-cycloadduct as **15** has yet been isolated in any reaction of diazoketone with nitrosobenzene.[9]



Experimental

All the melting points are uncorrected. Photolysis was carried out at room temperature under a nitrogen atmosphere, using light from a 100-W high-pressure mercury lamp (Riko Kagaku Sangyo Co), with filtered Pyrex glass. The IR, UV, and NMR spectra were measured in a KBr disk, $CHCl_3$, and $CDCl_3$ respectively, unless otherwise stated. The mass spectra were obtained with an ionization energy of 75 eV.

Preparation of Diazo Ketone (2). A mixture of 3,4-bis(diphenylmethylene)cyclobutanedione[3] (4.12 g, 10 mmol), tosylhydrazine (2.05 g, 11 mmol), and concd HCl (1 ml) in CH_2Cl_2–MeOH (1: 1, 200 ml) was kept at room temperature for 4 h. The crude crystals thus formed were recrystallized from AcOEt to give **1** as red needles; 5.80 g (100%); mp 145—146 °C. IR (Nujol): 3240 (NH), 1750 (C=O), 1170 (SO_2), 755 cm^{-1} (Ph); λ_{max}: 281 (28000), 398 (24000), 440 sh (8400), 515 nm (ε, 10000); NMR: 0.10 (s, 1H, NH), 2.35—2.9 (m, 14H), 3.17 (s, 5H), 3.24 (s, 5H), 7.62 τ (s, 3H).

Found: C, 76.46; H, 4.53%. Calcd for $C_{37}H_{28}O_3N_2S$: C, 76.54; H, 4.86%.

To a stirred solution of **1** (1.16 g, 2 mmol) in $CHCl_3$ (50 ml), we added aluminum oxide (20 g, Woelm, basic activity I) at 0 °C over a period of 30 min; the stirring was continued for a further hour. The mixture was then passed through the short column packed with basic aluminum oxide (30 g) described above, using $CHCl_3$ (200 ml) as the eluent. The crude crystals left after the evaporation of the solvent were recrystallized from ether-light petroleum to afford **2** as orange prisms; 0.81 g (95%); mp 123—124 °C. IR: 2050 (N_2), 1745 cm^{-1} (C=O); λ_{max}: 262 (10000), 271 (11000), 338 (6700), 420 nm (ε, 5100).

Found: C, 84.65; H, 4.60%. Calcd for $C_{30}H_{20}ON_2$: C, 84.88; H, 4.75%.

Photolysis of **2** *in the Presence of Alcohols, Aniline, and Water.* A mixture of **2** (424 mg, 1 mmol) and MeOH (20 ml) in benzene (150 ml) was irradiated for 2 h. The oily material left after the evaporation of the solvent was chromatographed on silica gel, using benzene as the eluent, to afford crude crystals. The recrystallization from EtOH afforded **5a** as colorless prisms; 372 mg (87%). The photochemical reactions of **2** with EtOH, *i*-PrOH, and aniline, according to the same procedure as above, afforded **5b**, **5c**, and **5e** respectively. The photochemical reaction of **2** with water was carried out in dioxane for 12 h. The oily material left after the evaporation of the solvent was taken up in ether, from which **5d** was extracted with an aqueous Na_2CO_3 solution. The physical properties, yields, and analytical data of **5a**—**e** are summarized in Table 1.

Thermal Reaction of **2** *in Aqueous Dioxane.* A solution of **2** (424 mg, 1 mmol) in 10%-aqueous dioxane (30 ml) was refluxed for 1 h. The reaction mixture was then treated by the procedure used for the reaction mixture of the photolysis of **2** in aqueous dioxane to afford **5d**; 215 mg (52%).

Reduction of **5a** *with* $LiAlH_4$. To a stirred solution of **5a** (200 mg, 0.47 mmol) in ether (20 ml), we added an excess of $LiAlH_4$. The reaction mixture was stirred for a further hour, decomposed with dil-HCl, and then extracted with ether. The crude crystals left after the evaporation of the solvent were recrystallized from CH_2Cl_2–EtOH to give **6** as colorless prisms; 180 mg (95%); mp 141—142 °C. IR (Nujol): 3400 and 1070 cm^{-1} (OH); λ_{max} 260 (23700), 375 nm (ε, 28600); NMR; 2.48 (s, 10H), 3.05 (s, 5H), 3.12 (s, 5H), 6.03 (d, J=9 Hz, 2H), 7.13 (t, J=9 Hz, 1H), 8.75 τ (br s, 1H, OH).

Found: C, 89.65; H, 5.88%. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04%.

Chlorination of 6 with $SOCl_2$. To a solution of 6 (100 mg, 0.25 mmol) in ether (10 ml), we added an excess of $SOCl_2$, after which the mixture was refluxed for 1 h. The oily material left after the evaporation of the solvent was chromatographed on silica gel, using benzene as the eluent, to give **7** as orange prisms; 42 mg (40%); mp 183—184 °C. NMR: 2.60 (s, 5H), 2.65 (s, 5H), 3.07 (s, 10H), 4.83 (t, J=5.5 Hz, 1H), 6.55—67.5 τ (m, 2H).

Found: C, 85.87; H, 5.42%. Calcd for $C_{30}H_{23}Cl$: C, 86.00; H, 5.53%. The spectral data of **7** were identical with those of an authentic sample prepared by the addition of HCl to 3,4-bis(diphenylmethylene)-1-cyclobutene.[4]

Preparation of **9**. A solution of **2** (424 mg, 1 mmol) and azobenzene (200 mg, 1.1 mmol) in benzene (150 ml) was irradiated for 10 h. The oily material left after the evaporation of the solvent was chromatographed on silica gel. Elution with benzene afforded **9** as yellow prisms; 435 mg (75%); mp 186.5—187 °C. IR: 1760 cm^{-1} (C=O); λ_{max}: 270 (27200), 404 nm (ε, 28000); NMR: 2.30—3.40 (m); MS: *m/e* (rel intensity) 578 (M$^+$, 91), 501 (80), 459 (M$^+$—PhNCO, 34), 167 (100).

Found: C, 86.88; H, 5.15%. Calcd for $C_{42}H_{30}ON_2$: C, 87.17; H, 5.23%.

Preparation of **11** *and Its Hydrolysis.* A solution of **9** (580 mg, 1 mmol) in xylene (30 ml) was refluxed for 4 h. The subsequent evaporation of the solvent under reduced pressure afforded **11** as a red liquid; 460 mg (100%). IR (neat): 1600 and 1030 cm^{-1} (C–N); λ_{max}: 272 (37500), 395 nm (ε, 32000); NMR: 2.45—3.30 (m). **11** is very sensitive to water and is easily hydrolyzed. For example, when a solution of **11** (230 mg, 0.5 mmol) in AcOEt (10 ml) was kept at room temperature for 1 day, **12** was obtained as colorless prisms after recrystallization from AcOEt; 180 mg (75%); mp 224—225 °C. IR (Nujol): 3330, 1655, and 1520 cm^{-1} (CONH); λ_{max}: 245 (21200), 337 nm (ε, 14000); NMR: 2.30—2.95 (m, 25H), 3.32 τ (br s, 2H); MS: *m/e* (rel intensity) 477 (M$^+$, 56), 385 (M$^+$—PhNH, 76), 357 (M$^+$—PhNHCO, 74), 279 (100).

Found: C, 87.85; H, 5.70%. Calcd for $C_{35}H_{27}ON$: C, 88.02; H, 5.70%.

Preparation of **10a**. *By Photolysis*: A solution of **2** (424 mg, 1 mmol) and *N*-benzylideneaniline (200 mg, 1.1 mmol) in benzene (150 ml) was irradiated for 8 h. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **10a** as yellow prisms; 376 mg (65%); mp 190—191 °C. IR: 1750 and 1260 (C=O), 1170 cm^{-1} (C–N); 2.35—3.7 (m, 30H), 4.68 τ (s, 1H); λ_{max}: 260 (36200), 383 nm (ε, 29500); MS: *m/e* (rel intensity) 578 (M$^+$, 20), 459 (M$^+$—PhNCO, 20), 397 (M$^+$—PhCH=NPh, 80), 396 (100).

Found: C, 89.10; H, 5.22%. Calcd for $C_{43}H_{31}ON$: C, 89.40; H, 5.41%.

By Thermolysis: A solution of **2** (424 mg, 1 mmol) and *N*-benzylideneaniline (200 mg, 1.1 mmol) in dioxane (30 ml) was heated under reflux for 1 h; thereafter it was worked up in a manner similar to that described above to afford **10a**; 237 mg (41%).

Preparation of **10b**. *By Photolysis*: A solution of **2** (424 mg, 1 mmol) and *N*-(diphenylmethylene)aniline (314 mg, 1.1 mmol) in benzne (150 ml) was irradiated for 10 h. The oily material left after the evaporation of the solvent was chromatographed on silica gel, using benzene as the eluent, to give **10b** as yellow prisms; 530 mg (81%); mp 242—246 °C. IR: 1740 and 1250 (C=O), 1170 (C–N), 740 cm^{-1} (Ph); λ_{max}: 263 (30000), 383 nm (ε, 23900); MS: *m/e* 653 (M$^+$, 100), 396 (M$^+$—Ph_2C–NPh, 30), 291 (70).

Found: C, 89.75; H, 5.38%. Calcd for $C_{49}H_{35}ON$: C, 90.01; H, 5.40%.

By Thermolysis: A solution of 2 (424 mg, 1 mmol) and *N*-(diphenylmethylene)aniline (314 mg, 1.1 mmol) in dioxane (30 ml) was refluxed for 1 h. The oily material left after the evaporation of the solvent was chromatographed on silica gel, using benzene as the eluent, to afford **10b**, 260 mg (40%).

Preparation of **13**. *By Photolysis*: A solution of **2** (424 mg, 1 mmol) and *p*-benzoquinone (126 mg, 1.1 mmol) in benzene (150 ml) was irradiated for 6 h. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to give **13** as yellow prisms; 227 mg (45%); mp 218.5—220 °C. IR: 1760 and 1670 cm^{-1} (C=O); λ_{max}: 246 (25400), 265 (22600), 350 (14000), 455 nm (ε, 7400)0 NMR: 2.54 (s, 10H), 3.00 (s, 5H), 3.17 (s, 5H), 3.35 (s, 2H), 7.13 τ (s, 2H); MS; *m/e* (rel intensity) 504 (M$^+$, 100), 427 (M$^+$—Ph, 20).

Found: C, 85.49; H, 4.98%. Calcd for $C_{36}H_{24}O_3$: C, 85.69; H, 4.79%.

By Thermolysis: A solution of **2** (424 mg, 1 mmol) and *p*-benzoquinone (126 mg, 1.1 mmol) in dioxane (30 ml) was refluxed for 2 h. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **13**; 298 mg (59%).

Preparation of **14** *and Its Thermal Decomposition.* A solution of 2 (424 mg, 1 mmol) and *p*-benzoquinone (126 mg, 1.2 mmol) in benzene (30 ml) was kept for 12 h at 0 °C. The crude crystals left after the evapotation of the solvent were recrystallized from CH_2Cl_2–EtOH to afford **14** as orange prisms; 425 mg (80%); mp 290 °C. IR: 1760 and 1695 cm^{-1} (C=O); λ_{max}: 283 (26000), 362 (17000), 450 nm (ε, 10000);

NMR: 2.25—3.7 (m, 22H), 7.40 τ(s, 2H).

Found: C, 80.94; H, 4.28%. Calcd for $C_{36}H_{24}O_3N_2$: C, 81.18; H, 4.54%.

A solution of **14** (200 mg, 0.38 mmol) in xylene (50 ml) was heated at reflux for 4 h. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **13**; 180 mg (95%).

*Preparation of **15** and **16**.* A solution of **2** (848 mg, 2 mmol) and nitrosobenzene (630 mg, 4 mmol) in benzene (50 ml) was kept for 10 h at room temperature. The crude crystals left after the evaporation of the solvent were recrystallized from CH_2Cl_2–EtOH to afford a mixture of pale yellow (**15**; 160 mg (15%); mp 120 °C dec) and brilliant black crystals (**16**; 475 mg (50%); mp 211—213 °C), which were separated mechanically. When a solution of the former (**15**, 100 mg, 0.19 mmol) in AcOEt was heated at reflux for 10 min and then kept for 12 h, the latter crystals were obtained; they were subsequently recrystallized from AcOEt to afford **16**; 76 mg (80%) **15**. IR: 1780 (C=O), 1195 cm^{-1} (C–N); λ_{max}: 242 (27000), 315 nm (ε, 14500); NMR: 2.35—2.75 (m, 10H), 2.85—2.95 (m, 5H), 3.0—3.4 τ (m, 10H).

Found: C, 80.92; H, 4.48%. Calcd for $C_{36}H_{25}O_2N_3$: C, 81.33; H, 4.74%.

16. IR: 1750 (C=O), 1290 cm^{-1} (N–O); λ_{max} 241 (17200), 280 (16300), 408 (10000), 505 (11700), 585 sh (3700), 640 nm (ε, 2300); MS: *m/e* (rel intensity) 503 (M$^+$, 9), 487 (M$^+$—O, 28), 382 (67), 189 (100).

Found: C, 85.60; H, 5.12%. Calcd for $C_{36}H_{25}O_2N$: C, 85.86; H, 5.00%.

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