Eu(fod)$_3$ (0.248 g, 0.00024 mol, molar ratio of shift reagent to alcohol 0.235) was prepared. The description of the nmr spectrum of that solution follows.

Nmr −2.70 [Eu(fod)$_3$ protons], −1.47, m (1.7 H), −0.74, m (5.1 H), 0.0–1.4, m (8.9 H, 1.88, AB d (1.3 H), 2.47, AB d (0.6 H), 2.8–3.7, m (4.0 H), 4.27, broad s (0.5 H), 5.00, d (0.5 H, J = 13–14 Hz), 7.40, m (1.0 H), 9.20 ppm, m (0.5 H). Irradiation at 9.20 ppm yields a doublet at 2.47 ppm (J = 13.5 Hz). Irradiation at 1.88 ppm yields a broad singlet at 7.40 ppm, and the coalescence of two peaks (J = 13 Hz) in the 2.8–3.7-ppm multiplet to a singlet. Irradiation at 3.30 ppm yields a broad singlet at 1.15 ppm (collapse of doublet, J = 12 Hz), and the collapse of a doublet (J = 12 Hz) at 0.40 ppm.

B. *Via* **Lithium Aluminum Hydride, Mixture D. 10** (1.05 g, 0.00772 mol) in 10 ml of dry ether was added dropwise to a stirred suspension of lithium aluminum hydride (0.15 g, 0.00395 mol) in 10 ml of dry ether. After addition was complete, the mixture was stirred for an additional 15 min, then cooled in an ice-water bath. Water and wet sodium sulfate were added, and the layers were separated. The water layer was washed with an additional 20 ml of ether, and the combined ether layers were washed with water and saturated sodium chloride solution. The ether layer was dried over anhydrous potassium carbonate and solvent was removed *in vacuo*. The product was recrystallized from pentane, yield 0.80 g (75%), mp 158–163°. The nmr spectrum of this mixture in the presence of Eu(fod)$_3$ (0.35 equiv) was similar to that of the mixture produced *via* hydroboration–oxidation (see mixture A); the ratio of exo,endo to exo,exo alcohol was 2.0:1.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by funds from an Institutional Grant from the National Science Foundation to New York University. Grateful acknowledgment is made to the donors of these funds.

Registry No.—**1**, 7092-05-9; **2**, 51260-33-4; **3**, 51260-38-9; **4**, 51260-34-5; **5**, 944-41-2; **6**, 51175-60-1; **7**, 27019-94-9; **8**, 51260-36-7; **9**, 51260-35-6; **10**, 51260-37-8; 3-chloropropene, 107-05-1; 1,3-cyclohexadiene, 592-57-4; maleic anhydride, 108-31-6; cycloheptatriene, 544-25-2; *exo*-tricyclo[3.2.2.0^{2,4}]nonane-*exo*-6,*exo*-7-dicarboxylic anhydride, 944-40-1.

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(2) (a) National Science Foundation Trainee, 1965–1966; Summer Trainee, 1967, 1970. (b) This work is taken in part from the Ph.D. Dissertation of P. E. S., 1972. (c) On sabbatical leave at the Universität Freiburg, Freiburg im Breisgau, West Germany, 1972–1973. (d) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, Abstracts of Papers, ORGN 129.

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(5) These and other bi- and tricyclic systems have been named according to a system suggested by Dr. K. L. Loening, Director of Nomenclature of the Chemical Abstracts Service of the American Chemical Society. The carbon bridge bearing the highest locants is taken as the reference bridge, to which *first the cyclopropane* (considered as a substituent) and *then the alcohol* moieties are referred, using the Beilstein exo–endo system (see Introduction to "Beilstein's Handbuch der Organischen Chemie," 3rd Supplement, Vol. 6, Part 4, Springer-Verlag, West Berlin, 1966). The authors gratefully acknowledge the assistance of Dr. Loening in this matter.

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(24) The hydroxyl proton is invariably shifted too far downfield at these relative concentrations to be observed.[22]

(25) Obtained from Winthrop Laboratories, Inc.

(26) We gratefully acknowledge the generous gift of cycloheptatriene from the Shell Chemical Corp., Calif.

(27) Caution: desiccation under high vacuum for extended periods leads to substantial dehydration to the anhydride. Observation of R. Leight in this laboratory.

Conformational Analysis of Some Bicyclo[4.2.0]octanes by Hydrogen-1 Nuclear Magnetic Resonance

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7,7-Diphenyl-2,5-dioxabicyclo[4.2.0]octane (**1**), 7,7-diphenyl-2,5,8-trioxabicyclo[4.2.0]octane (**2**), and 7,7-dimethyl-2,5,8-trioxabicyclo[4.2.0]octane (**3**) were shown to exist as cis-fused chairs. The conformational analyses were accomplished by a combination of Eu(fod)$_3$ shift ratios and the Buys R method. The Eu(fod)$_3$ was shown to have no effect on the conformation. The bicyclooctanes were synthesized through the photocycloaddition of acetone, benzophenone, and 1,1-diphenylethylene to 1,4-dioxene.

Buys[2] and Lambert[3] have developed methods for determining the conformation of rigid six-membered ring systems, containing heteroatoms in the 1 and 4 positions, by nmr. These methods relate the ratio of the average trans and cis vicinal coupling constants to the conformation.

Slessor and Tracy[4] have written a computer program, Dihedral Angle Estimation by the Ratio Method (DAERM), for the conformational analysis of a CHR_2CH_2R system. This method is based on the assumption that the ratio of Karplus constants for the cis and trans dihedral angles is a constant (0.9). Conformational analysis of some four-membered-ring compounds gave results consistent with those obtained by X-ray and dipole moment studies.[5]

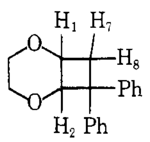
Simplification of complex spectra through the application of the shift reagent, Eu(fod)$_3$, is an established technique.[6] Compounds with two binding sites have been dealt with by Williams, *et al.*[7] They have shown that competition between sites can be detected by a plot of shift *vs.* the molar ratio of shift reagent to substrate.

These systems present the possibility of competition between various sites, some of which may be favored on steric considerations, others on electronic.

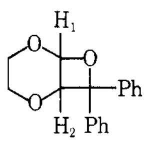
The conformations of the dioxane portion of compounds **1**-**3** were determined by Buys and Lambert's methods and the conformation of the cyclobutane portion of **1** by DAERM. The coupling constants were obtained from the Eu(fod)$_3$ shifted spectra and refined through the program NMRIT.[8]

Results and Discussion

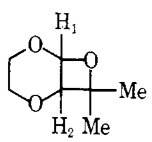
The 60-MHz nmr spectra of compounds **1**-**3** are shown in Figure 1. The partial spectra for the oxetanes **2** and **3** consist of two doublets, for the bridgehead protons, and a complex four-spin pattern (ABCD) for the methylene protons. The spectrum of the cyclobutane **1** is composed of two independent four-spin sets, an ABCD pattern for the dioxane methylene portion and a first-order pattern for the cyclobutane protons. The protons at 4.95 ppm in the spectra of **1** and **2** are assigned to H-2. The protons at 5.53 and 5.63 ppm are assigned to H-1 of compound **2** and **3**, respectively; the remaining protons, compound **1**, 4.2 ppm, H-1, and compound **3**, 4.22 ppm, H-2.



1



2



3

The chemical shift difference between the A proton and the BCD envelop of the oxetanes **2** and **3** is attributed to the anisotropy of the oxetane ring. This difference is 25 Hz for compound **2** in deuteriochloroform, increasing to 45 Hz in hexadeuteriobenzene. These differences become 92 and 165 Hz ($\Delta\nu/J$, 8.4 and 15), respectively, at 220 MHz; however, this system is too strongly coupled for the A proton to become first order. The spectra of compounds **2** and **3** were simplified through the addition of the Eu(fod)$_3$ shift reagent.

The shifts of the bridgehead and methylene protons for compounds **1**-**3** were plotted against the molar ratio of Eu(fod)$_3$ to substrate. These plots gave straight lines, indicating that only one binding site was involved over the concentration range studied. Comparison of the slopes for H-1 and H-2 reveals that oxygen-5 does not complex the Eu(fod)$_3$, as expected in view of the steric hindrance of the R groups. Caple,[9] in a study of rigid bicyclic ethers, developed a model for the europium-ether complex in which europium lies in the C-O-C plane 3.0 Å from the oxygen and equidistant from the carbons. The slopes of H-1 and H-4 for the cyclobutane **1** are consistent with this model (refer to A (**1** and **2**) and B for proton numbering system). However, for the oxetanes **2** and **3**, the slopes for H-1 are greater than those for either H-3 or H-4. The binding site for oxetanes **2** and **3** apparently consists of oxygen-2 and oxygen-8. While it is impossible from our data to differentiate between a bidentate complex, a, and the time average of two 1:1 complexes, b, a model in which the europium lies equidistant (3.0 Å) from both oxygens and close to the intersection of the C-O-C planes of the oxetane and dioxane rings is consistent with the data.

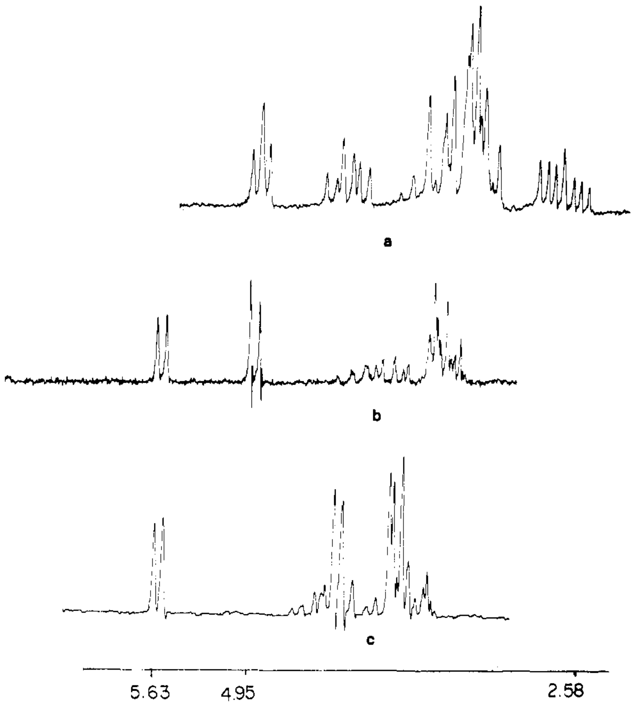
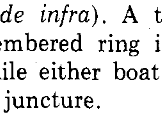
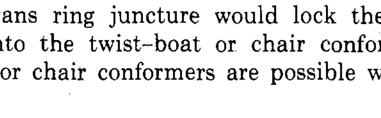


Figure 1. Partial 60-MHz nmr spectra: (a) 7,7-diphenyl-2,5-dioxabicyclo[4.2.0]octane (**1**); (b) 7,7-diphenyl-2,5,8-trioxabicyclo[4.2.0]octane (**2**); (c) 7,7-dimethyl-2,5,8-trioxabicyclo[4.2.0]octane (**3**).



a



b

As a result of the synthetic method, the ring juncture in the bicyclo[4.2.0]octane systems may be either cis or trans (*vide infra*). A trans ring juncture would lock the six-membered ring into the twist-boat or chair conformers while either boat or chair conformers are possible with a cis juncture.

Examination of Dreiding models of the complexes (*vide supra*) for the various conformations of the bicyclooctanes revealed that a trans ring juncture would require H-2 to have a greater shift than either H-3 or H-4. Since this was not observed in these systems, the trans ring juncture can be excluded. The band widths in the europium simplified, first-order spectra (25 and 16 Hz) demonstrate that the dioxane rings exist in the chair conformation.

In the 60-MHz spectra the BCD envelopes for compounds **1**-**3** are approximately 25 Hz wide; therefore, the chemical shift differences for these protons are less than 25 Hz. After the addition of Eu(fod)$_3$, these protons are separated by at least 25 Hz in the first-order spectra; therefore, the relative shift orders can be obtained directly. The decreasing proton shift orders follow: cyclobutane **1** (4, 3, 5, 6); diphenyloxetane **2** (3, 4, 5, 6); and dimethyloxetane **3** (5, 3, 4, 6).

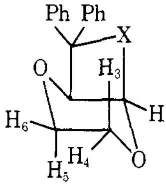
Correlation of these empirical shift orders and the slopes from a least-squares treatment of the chemical shift *vs.* the molar ratio of europium reagent to substrate demonstrates that the cyclobutane **1** and the diphenyloxetane

Table I
NMRIT Refined Coupling Constants for Compounds 1–3

	Coupling constants, Hz										
Compd	1,2	1,7	1,8	2,7	2,8	3,4	3,5	3,6	4,5	4,6	5,6
1	3.66[a]	7.7[a]	6.74[a]	0.0[a]	−3.78[a]	−12.36	9.68	2.15	2.11	1.34	−12.15
2						−12.39	10.85	2.36	2.41	2.34	−12.08
2[b]	4.0					−11.61	11.0	1.73	2.45	2.11	−12.14
3	4.0					−11.43	11.53	2.22	2.27	0.95	−12.20

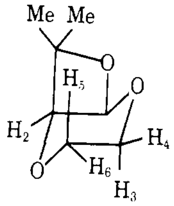
[a] Confirmed by spin decoupling, $J_{7,8} = -10.96$ Hz. [b] Calculated for uncomplexed diphenyloxetane **2**.

2 exist as the frozen chair conformer A and the dimethyloxetane 3 exists as the alternate conformer B.



A

1, X = CH_2
2, X = O



B

The assumption that $Eu(fod)_3$ will not affect the coupling constants is an accepted practice.[6] However, it was desired to demonstrate this by calculating the spectrum of the diphenyloxetane 2 in the absence of europium reagent. The (NMRIT[8]) refined values of the coupling constants from the europium-shifted spectra of 2 were used as input and the chemical shifts were adjusted by trial and error. The calculation was performed for the 220-MHz spectrum of 2 obtained in deuteriochloroform (Figure 2). The iterated solution approximates the experimental spectrum. The refined and calculated coupling constants are given in Table I.

A difference in the coupling constants obtained for the diphenyloxetane 2 from the europium-shifted spectrum and by calculation is evident in Table I. This deviation between solutions is believed to be a reflection of the precision of the method owing to inaccuracy in determining line positions in the experimental spectra. The main sources of the error are broadening by europium and hidden lines in the 220-MHz spectrum.

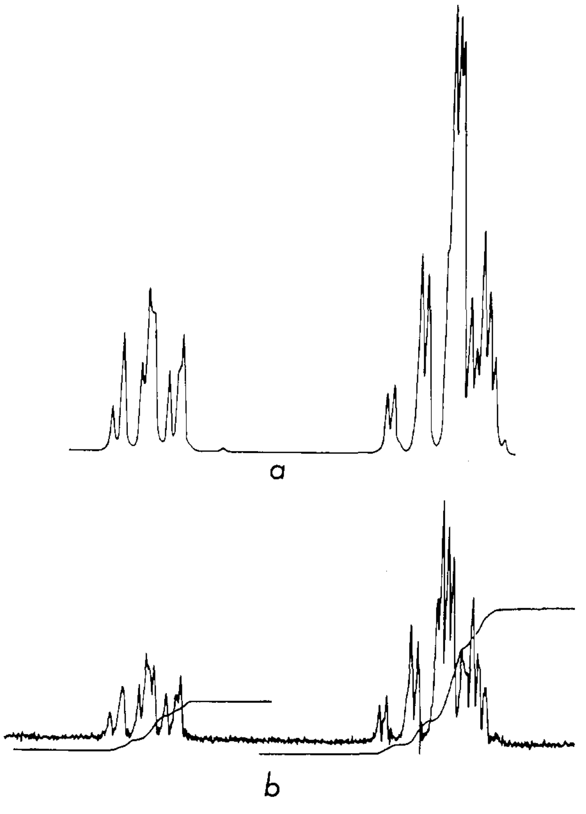


Figure 2. Partial 220-MHz nmr of 7,7-diphenyl-2,5,8-trioxabicyclo[4.2.0]octane (2): (a) calculated; (b) experimental in $CDCl_3$.

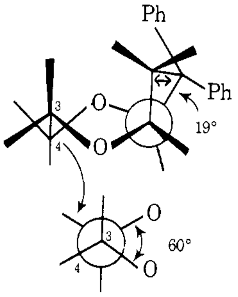
Table II
Calculated Ring Dihedral Angles ($O-CH_2-CH_2-O$) for Compounds 1–3 by Buys' *R* Method

Compd	*R*	Dihedral angle, deg
1[a]	2.59	60
2	2.79	61
2[b]	2.82	62
3	2.78	61

[a] A cyclobutane dihedral angle of 19° was calculated by the Slessor and Tracy method: $\omega = 127.6°$, $K/K' = 0.9$. [b] 220-MHz spectrum of diphenyloxetane **2**.

While the coupling constants calculated for the uncomplexed 220-MHz spectrum and the europium-shifted spectrum of the diphenyloxetane 2 differ by as much as 0.6 Hz for the axial–equatorial coupling constant, the dihedral angles obtained from the Buys *R* method (Table II) differ only by the nominal value of one degree. Therefore, conformational insensitivity to the europium reagent has been confirmed for this system.

The conformation of the cyclobutane 1 is shown by 1a.



1a

The Karplus constant calculated by DAERM for the ring juncture in the cyclobutane is 4.41 Hz. Solution of the Karplus equation using this value gives a dihedral angle of 9.9° for the oxetanes. However, the variation of the Karplus constant with electronegativity and orientation of substituents has been established.[10] This variation is demonstrated in the cyclobutane by a Karplus constant of 4.41 Hz for the H_1–C–C–H_2 dihedral angle and 8.97 Hz for the H_1–C–C–H_7 dihedral angle. Since it is impossible to estimate the effect of the oxetane oxygen on the Karplus constant for the H_1–C–C–H_2 dihedral angle, the value of 9.9°, calculated with a Karplus constant of 4.41 from the cyclobutane, is a qualitative estimate at best. It has been shown that oxetanes have a greater tendency for planarity than cyclobutanes;[11] therefore, the cyclobutane dihedral angle of 19° is probably a reasonable upper limit for the dihedral angle in the oxetanes.

Stereospecificity. The photocycloadditions of benzophenone, 1,1-diphenylethylene, and acetone to olefins have been examined.[12-14]

The intermediacy of the triplet state of benzophenone in the Paterno-Buchii reaction has been established.[12] In addition Servé has shown by quenching experiments that the triplet state of 1,1-diphenylethylene is involved in the formation of 7,7-diphenyl-2-oxabicyclo[4.2.0]octane.[13] However, the expected mixture of cycloadducts with cis and trans ring junctures was not obtained in the present cases.

Turro, *et al.*,[14] have shown that singlet as well as triplet mechanisms may operate in oxetane formation from acetone and enol ethers. Thus, the cis-fused 7,7-dimethyl-2,5,8-trioxabicyclo[4.2.0]octane (**3**) could be explained by a singlet mechanism. However, the factors which resulted in the isolation of only cis-fused 6:4 ring systems, by an apparent triplet mechanism, are not clear. Examination of the crude reaction mixtures did not reveal the presence of additional isomers.

Summary. The bicyclooctanes **1-3** have been shown to be amenable to europium shift reagent simplification and the coupling constants have been calculated by the programs NMRIT and NMREN1.[8] The presence of the phenyl substituent in the 7 positions of **1** provides sufficient steric hindrance to cause preferential complexation with the oxygen in the 2 position.

The anticipated distortion[15a] of the six-membered ring in a cis-fused 6:4 system is demonstrated by an R value range of 2.6-2.8, whereas a trans-fused ring would be expected to have R values less than 2.20.[15b]

Lambert's and Buys' methods have been applied to fused 6:4 ring systems[16] and in conjunction with Eu(fod)$_3$ shift data demonstrate the absolute conformation of these bicyclooctanes.

Experimental Section

General. Photolyses were conducted in an immersion well reactor with a 450-W Hanovia medium-pressure mercury lamp fitted with a Pyrex filter sleeve and in a Srinivasan-Griffin reactor. The reactions were run with a nitrogen sweep. The nitrogen was bubbled through a vanadyl sulfate solution to remove oxygen.[17]

The nmr spectra were determined on Varian Associates A-60, HA-100, and HR-220 MHz spectrometers. The spectra were determined in deuteriochloroform or hexadeuteriobenzene with tetramethylsilane as an internal standard. Infrared spectra were determined with a Perkin-Elmer 337 grating infrared spectrometer on chloroform solutions or KBr disks. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Micro-Analysis, Inc., Wilmington, Del. All melting points are uncorrected. Eu(fod)$_3$ was purified by sublimation and transfers were made in a nitrogen atmosphere. The theoretical calculations were performed on IBM 370-165 and IBM 360-70 computers.

Synthesis of 7,7-Diphenyl-2,5-dioxabicyclo[4.2.0]octane (1). Dioxene (1.025 g, 0.012 mol) and 1,1-diphenylethylene (2.115 g, 0.012 mol) were dissolved in 50 ml of thiophene-free benzene and irradiated at 3000 Å in a Srinivasan-Griffin reactor for 69.5 hr. The solvent was removed under vacuum on a rotary evaporator and the residue was chromatographed on a 20 × 3 cm column containing 20 g of silica gel. The column was eluted with 50 ml of low-boiling petroleum ether-benzene (3:1), 50 ml of benzene, and 50 ml of benzene-chloroform (3:1) to yield a tacky white solid which sublimed at 80° (0.1 mm), giving 0.3 g (10% yield) of **1**: mp 83.5-84.5°; ir (KBr) 3048, 3030, 2985, 2959, 2907, 2849, 1594, 1490, 1447, 1389, 1370, 1284, 1250, 1235, 1163, 1149, 1136, 1093, 1070, 1001, 943, 893, 774, 876, 844, 704, 650, and 617 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77; mol wt, 254. Found: C, 81.29; H, 6.93; mol wt, 256 (benzene).

Synthesis of 7,7-Diphenyl-2,5,8-trioxabicyclo[4.2.0]octane (2). Dioxene (3.174 g, 0.037 mol) and benzophenone (6.67 g, 0.037 mol) were dissolved in 600 ml of thiophene-free benzene. The solution was irradiated in a Hanovia immersion well photoreactor fitted with condenser and nitrogen sweep for 34 hr (92% consumption of dioxene by glc). The solvent was removed under vacuum on a rotary evaporator, yielding 7.443 g (82%) of **2** as white crystals. The solid was recrystallized from chloroform and then from ethyl acetate: mp 145-146°; ir (KBr) 3049, 3030, 2985, 1594, 1488, 1447, 1399, 1379, 1294, 1269, 1235, 1160, 1087, 1044, 1001, 928, 870, 793, 769, 749, 723, 707, 694, 658, and 641 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.12; H, 6.01. Found: 76.05; H, 6.12.

Synthesis of 7,7-Dimethyl-2,5,8-trioxabicyclo[4.2.0]octane (3). A solution of dioxene (2.12 g, 0.25 mol) in 600 ml of reagent-grade acetone was placed in the immersion well photoreactor fitted with a condenser and nitrogen sweep. The mixture was irradiated for 5 days. The acetone was removed under vacuum on a rotary evaporator and the product was distilled to give a clear, colorless liquid which solidified in the receiver: bp 44° (1.0 mm); yield 2.36 g (66%); ir ($CHCl_3$) 2985, 2963, 2933, 2874, 1455, 1404, 1381, 1368, 1297, 1282, 1259, 1223, 1170, 1146, 1108, 1042, 995, 976, 946, 926, 909, 879, and 844 cm^{-1}.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.33; H, 8.33; O, 33.33. Found: C, 57.96; H, 8.27; O, 33.31.

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Registry No.—**1**, 51175-63-4; **2**, 51175-64-5; **3**, 51175-65-6; dioxene, 543-75-9; 1,1-diphenylethylene, 530-40-3; benzophenone, 119-61-9; acetone, 67-64-1.

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