Synthesis and Chemistry of a Bicyclobutane-Bridged α-Diazo Ketone[1]

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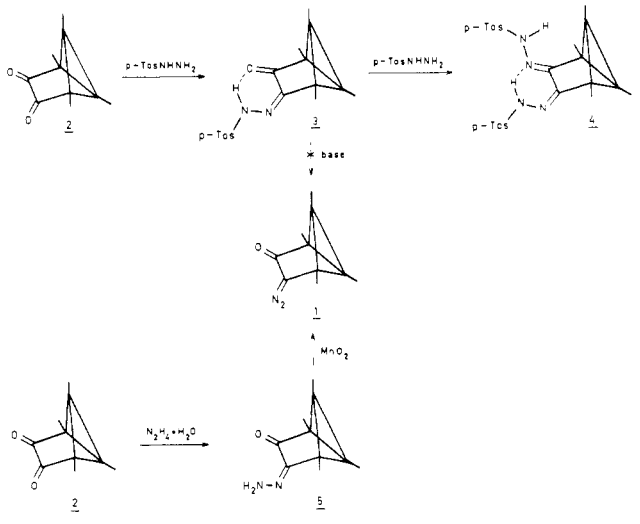
The preparation and a number of reactions of the bicyclobutane-bridged α-diazo ketone **1** are reported. The 1,3-dipolar addition of **1** to activated unsaturated carbon–carbon bonds affords heterocyclics with an intact bicyclobutane ring system. This is exemplified by the reaction of **1** with enone **8** to give pyrazoline **9** which provides upon photolytically or thermally induced extrusion of nitrogen the bis(bicyclobutane)-substituted cyclopropane **16**. Compound **16** isomerizes thermally to dihydrobenzofuran derivative **17**, which is an example of a cyclopropyl ketone–dihydrofuran rearrangement. Also, some reactions of **1** involving loss of nitrogen were investigated. The transition-metal-catalyzed decomposition of **1** in methanol leads to mixtures of phenol **24** and 2,5-cyclohexadienone **25**. The $AgClO_4$-catalyzed decomposition of **1** in the presence of electron-rich alkenes affords aromatic adducts, arising from a (formal) 1,3-dipolar addition of the α-keto carbenoid species to the alkene, whereas the analogous reaction with $Rh_2(OAc)_4$ furnishes **47**, resulting from (formal) dimerization of the α-keto carbenoid with incorporation of an oxygen atom. The reaction of **1** with tetrachloro-*o*-quinone leads to formation of **23** in which the bicyclobutane moiety has remained intact; on the other hand, treatment of **1** with *o*-dihydroxybenzene provides a mixture of the rearranged adducts **49** and **51**. Finally, the preparation and some properties of bis(tosylhydrazone) **4** are described.

α-Diazo ketones can be put to diverse uses in organic synthesis.[2a] For example, the 1,3-dipolar addition to activated alkenes and alkynes affords pyrazolines and pyrazolenines, respectively. Loss of nitrogen from the diazo ketone, either thermally, photochemically, or catalytically (transition metal), provides an α-keto carbene (or carbenoid) that may either display the well-known Wolff rearrangement[2a-c,3,4] leading to ketenes or be trapped, for instance, by alkenes to yield α-ketocyclopropanes[2a] or dihydrofuran derivatives, the latter resulting from a (formal) 1,3 dipolar addition.[2a,d] Upon treatment of diazo ketones with acid, products are obtained that result from the intermediate α-keto carbonium ion, which is generated from the initially formed diazonium ion by loss of nitrogen.[2e,f,5]

Strained-ring systems, especially bicyclobutane-bridged functionalities, are the subject of study in our laboratory.[6,7] Within this context we undertook an investigation of the chemistry of α-diazo ketone **1** which possesses the interesting features of a bicyclobutane fragment bridged on the 2,4-positions with the α-diazo ketone moiety. It was anticipated that diazo ketone **1** might be a useful precursor for the synthesis of other bicyclobutane-comprising compounds; on the other hand, it would be of interest to examine whether rearrangements of the sensitive, highly strained moiety would occur during some of the reactions. In particular, diazo ketone **1** was considered to be an appropriate precursor for the corresponding α-keto carbene and α-keto carbonium ion, the behavior of which was of importance for a comparison with the related bicyclobutylcarbinyl radical,[8] cation,[9] and anion.[10]

Scheme I



Results and Discussion

Bicyclobutane-Bridged Bis(tosylhydrazone) 4. The first route that was attempted for a synthesis of diazo ketone **1** involved the reaction of diketone **2**[6] with tosylhydrazine[2g] (Scheme I). The tosylhydrazone **3** that formed, upon treatment with base, was either recovered unchanged or decomposed into a complicated mixture of products, in which compound **1** could not be identified. Upon treatment of diketone **2** with 2 equiv of tosylhydrazine, bis(tosylhydrazone) **4** was obtained (60% yield).

From NMR spectroscopic evidence (see Experimental Section) it is clear that bis(tosylhydrazone) **4** exists in solution only as one isomer with the *Z,E* geometry. This is probably due to stabilization by intramolecular hydrogen bond formation as has been reported for similar diphenylhydrazones and osazones.[11] By analogy, tosylhydrazone **3** is assigned the *Z* geometry. An attempt was made to measure the barrier to *Z/E* isomerization around the C=N double bond by heating compound **4** in either Me_2SO-d_6 or *o*-dichlorobenzene solution. Up to 120 °C, where decomposition occurred, no line broadening of the

(1) This work has been the subject of a preliminary communication: J. Elzinga, R. F. Heldeweg, H. Hogeveen, and E. P. Schudde, *Tetrahedron Lett.*, 2107 (1978).

(2) (a) S. Patai, Ed., "The Chemistry of the Diazonium and Diazo Groups", Wiley, New York, 1978, Chapter 18, (b) p 612, (c) p 458, (d) p 896, (e) p 637, (f) Chapter 6, (g) pp 758–759, (h) p 580, (i) p 840, (j) p 437.

(3) (a) W. A. Kirmse, "Carbene Chemistry", Vol. I, 2nd ed., Academic Press, New York, 1971, p 475; (b) M. Jones, Jr., and R. A. Moss, Eds., "Carbenes", Vol. I, Wiley, New York, 1973, p 107.

(4) H. Meier and K. P. Zeller, *Angew. Chem.*, **87**, 52 (1975).

(5) R. A. More O'Ferral, *Adv. Phys. Org. Chem.*, **5**, 331 (1967).

(6) R. F. Heldeweg, H. Hogeveen, and E. P. Schudde, *J. Org. Chem.*, **43**, 1912 (1978).

(7) D. M. Kok, H. Hogeveen, and W. F. J. Huurdeman, *J. Am. Chem. Soc.*, **100**, 871 (1978).

(8) J. Elzinga and H. Hogeveen, *J. Org. Chem.*, **44**, 2381 (1979).

(9) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975); C. Giordano, R. F. Heldeweg, and H. Hogeveen, *J. Am. Chem. Soc.*, **99**, 5181 (1977); H. Hogeveen and L. Zwart, *J. Org. Chem.*, **44**, 1365 (1979).

(10) H. Hogeveen and L. Zwart, unpublished results.

(11) O. L. Chapman, R. W. King, W. J. Welstead, and T. J. Murphy, *J. Am. Chem. Soc.*, **86**, 4968 (1964).

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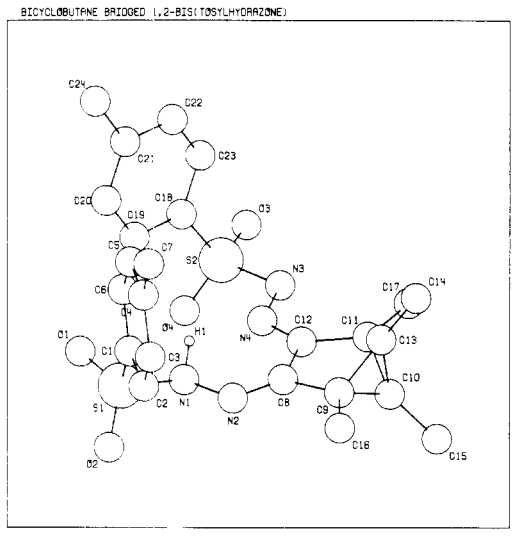
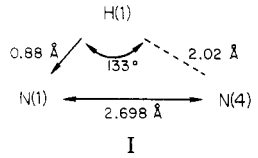


Figure 1. Structure of compound **4**.

^{1}H NMR absorptions due to the methyl groups of the tosyl and of the bicyclobutane moiety was observed. From these data the barrier to Z/E isomerization is calculated to be $\Delta G^{\ddagger}_{393} > 22$ kcal/mol.[12] It is of interest to note that substituted monohydrazones have also high (>30 kcal) inversion barriers.[13b]

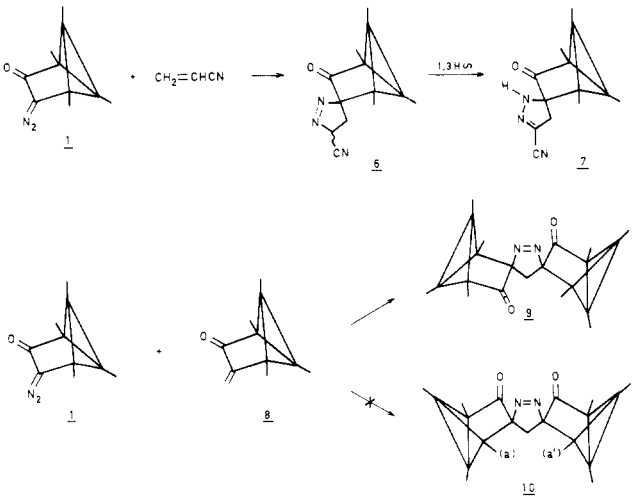
Although in one case an electron density projection of an osazone has been reported,[14] showing Z,E geometry to be present also in the crystalline state, a detailed X-ray structural analysis of a 1,2-dihydrazone had not been reported so far; therefore, the structure of **4** was subjected to an X-ray investigation performed by Spek.[15] The results[15] show unambiguously that also in the crystalline state compound **4** possesses the Z,E geometry (see Figure 1). It is noteworthy that the central part of the molecule, consisting of atoms C(8), C(9), C(11), C(12), N(1), N(2), N(3), and N(4), is almost flat. Atom H(1), covalently bonded to N(1) and hydrogen bonded to N(4), is not situated in this plane (which would be the most favorable situation for hydrogen bond formation), possibly due to steric hindrance between the phenyl groups. The relevant data concerning the intramolecular hydrogen bond are shown in structure I.[16]



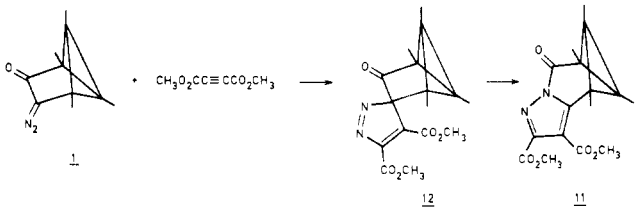
I

Bicyclobutane-Bridged α-Diazo Ketone 1. Synthesis. The route that proved to be convenient for the preparation of compound **1** involved hydrazone **5** which was obtained by treatment of diketone **2** with 1 equiv of hydrazine. The oxidation of **5** by the action of excess activated MnO_2 afforded 4-diazo-1,2,5,6-tetramethyltricyclo[3.1.0.0^{2,6}]hexan-3-one (**1**) in 60–80% overall yield as an orange oil, thermally unstable above 0 °C.

Scheme II



Scheme III

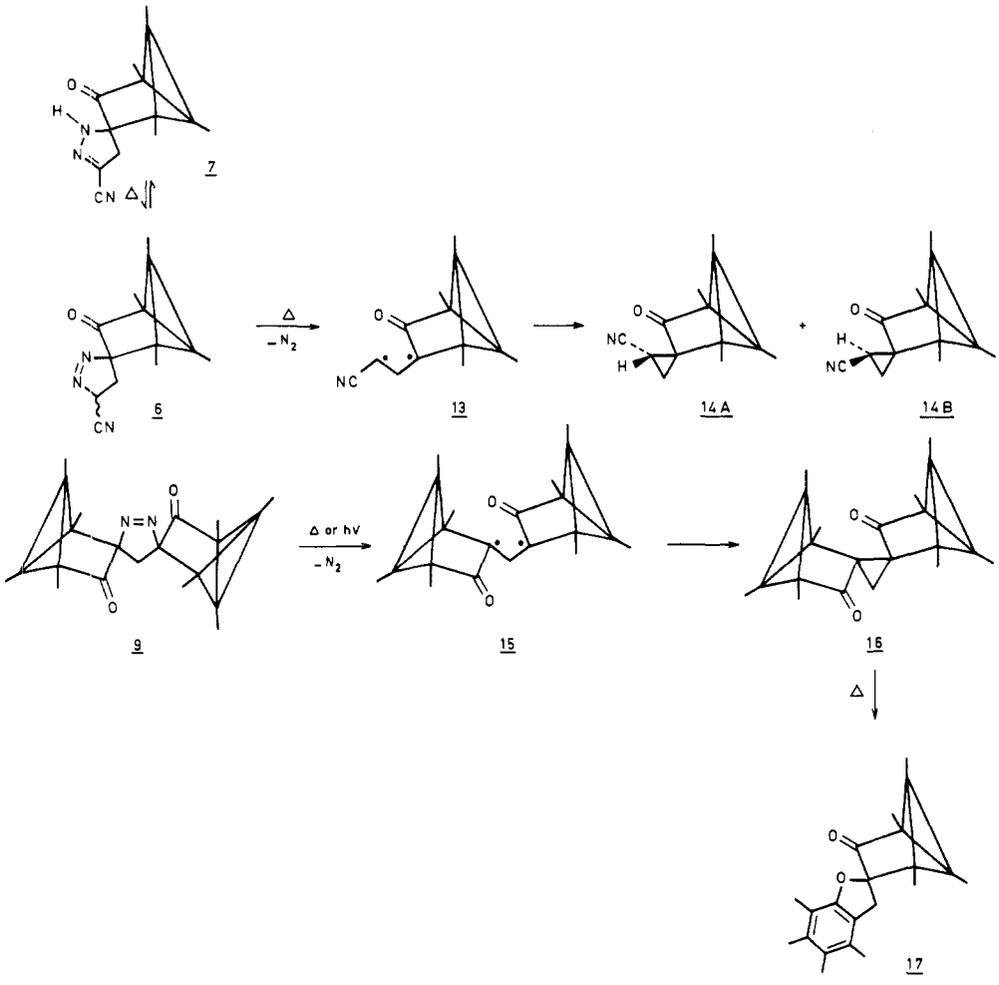


1,3-Dipolar Additions to Unsaturated Carbon–Carbon Bonds. The reaction of diazo ketone **1** with excess acrylonitrile provided Δ^2-pyrazoline **7** in almost quantitative yield. Indications for the intermediacy of Δ^1-pyrazoline **6** (Scheme II) were obtained by ^{1}H NMR spectroscopy: when compound **1** was mixed with acrylonitrile at −70 °C and the solution slowly warmed, the ^{1}H NMR spectrum recorded at −20 °C established the complete disappearance of **1**, and new singlets at δ 1.10, 1.20, 1.57, and 1.72 due to the methyl groups and ill-resolved multiplets in the region δ 1.0–2.2 (partially obscured by the methyl signals) were observed, consistent with structure **6**. While the sample warmed to room temperature the signals due to **6** decreased while those of **7** [absorptions at δ 1.13 (s, 3 H), 1.15 (s, 3 H), 1.50 (s, 3 H), 1.56 (s, 3 H), 2.90/2.80 (AB q, J = 15 Hz, 2 H), and 7.05 (s, NH)] appeared. The formation of **6** is consistent with the preferred orientation for [3 + 2] cycloadditions of diazo ketones:[2h,17] attack of the nucleophilic diazo-substituted carbon atom of **1** upon the electrophilic center in acrylonitrile.

The reaction of **1** with enone **8** afforded as the only product the *trans*-bis(bicyclobutyl ketone)-substituted pyrazoline **9** (85% yield), no cis isomer, **10**, being formed. The assignment of structure **9** (and not **10**) is based on the ^{1}H NMR spectrum which shows, in addition to the four methyl absorptions, a singlet for the CH_2 hydrogen atoms in all solvents used, e.g., at δ 1.35 in $CDCl_3$ solution. Also, in the presence of the shift reagent Eu(fod)$_3$ the CH_2 hydrogen atoms were observed as a sharp singlet; in structure **10** the CH_2 hydrogen atoms are diastereotopic and should have been observed as such. Hence, addition of **1** to **8** must proceed highly stereoselectively, owing probably to stereoelectronic factors: a comparison of the molecular models of both **9** and **10** shows that compound **10** will be disfavored by both steric crowding between the methyl groups a and a′ (see structure **10**) and by the electrostatic re-

(12) The $\Delta G^{\ddagger}$ was calculated from[13a] $\Delta G^{\ddagger} = 4.57T[10.32 + \log (T/k)]$.
(13) (a) H. Kessler, *Angew. Chem.*, **82**, 237 (1970); (b) H. O. Kalinowski, H. Kessler, D. Leibfritz, and H. Pfeffer, *Chem. Ber.*, **106**, 1023 (1973).
(14) K. Bjamer, S. Dahm, S. Furberg, and C. S. Petersen, *Acta Chem. Scand.*, **17**, 559 (1963); S. Furberg and C. S. Petersen, *Sel. Top. Struct. Chem.*, 83 (1967).
(15) A. L. Spek, *Cryst. Struct. Commun.*, **8**, 325 (1979).
(16) The corresponding data for L-histidine were found to be as follows: N↔N, 2.779 Å; N–H, 1.018 Å; N···H, 1.899 Å; N–H···N 142.8°. P. Schuster et al., Eds., "The Hydrogen Bond", Vol. II, North-Holland Publishing Co., Amsterdam, 1976, Chapter 8, Appendix.
(17) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); *ibid.*, **41**, 403 (1976).

Scheme IV



pulsion between the oxygen atoms in **10**.

Treatment of diazo ketone **1** with an activated alkyne, viz., dimethyl acetylenedicarboxylate, afforded an adduct in 57% yield which was identified as pyrazole **11** (Scheme III); the structure was recently confirmed by X-ray techniques.[18] Although not observed, we assume the intermediacy of pyrazolenine **12** arising from a 1,3-dipolar addition of **1** to the electron-deficient triple bond of dimethyl acetylenedicarboxylate which is followed by isomerization to pyrazole **11**. The isomerization involves a rapid [1,5] sigmatropic acyl migration analogous to those reported previously for pyrazolenines.[19]

In contrast to the above-mentioned reactions with electron-deficient alkenes, no reaction occurs upon treatment of **1** with electron-rich alkenes such as vinyl acetate and 2,3-dimethyl-2-butene; also, no reaction occurs upon treatment with electron-rich alkynes such as 2-butyne.

Thermal and Photochemical Decomposition of Pyrazolines 7 and 9. The thermally and photochemically induced extrusion of nitrogen from pyrazolines is a subject of extensive research from synthetic[2a,20,21] (formation of a three-membered ring) as well as from mechanistic points of view.[21-24] It is generally believed that in the thermal and photochemical decomposition of pyrazolines, biradicals are involved either as transition-state or as discrete intermediates.[20-24]

When Δ^2-pyrazoline **7** (Scheme IV) was boiled for 9 h in xylene solution, a mixture of the geometric isomers **14A,B** was obtained in 64% yield. This mixture was separated into the components by applying high-pressure LC; for the configurational assignment of the isomers, see below. Photolysis of **7** led to a complicated reaction mixture of several products, which were not isolated.

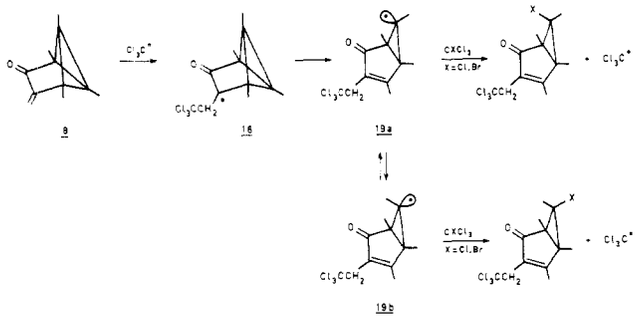
Upon irradiation of pyrazoline **9**, rapid loss of nitrogen took place to provide as the only isolated product the interesting bis(bicyclobutyl ketone)-substituted cyclopropane **16** in 65% yield. Upon heating of **9** at 120 °C, **16** was also formed, but it started to isomerize into dihydrobenzofuran **17** before complete conversion of **9** into **16** had occurred.

The ^{1}H NMR spectrum of **16** in various solvents and also in the presence of the shift reagent Eu(fod)$_3$ showed the cyclopropyl methylene hydrogen atoms to be identical (sharp singlet), which establishes the trans configuration for **16**.

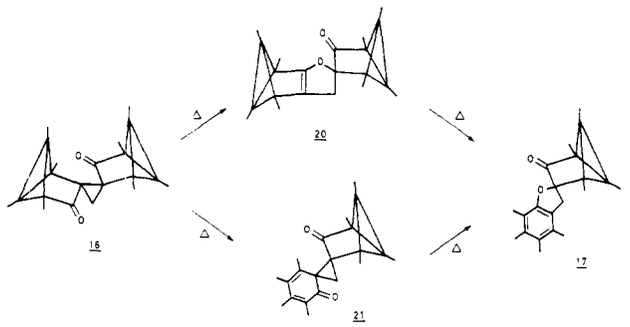
The formation of both **14A,B** and **16** from their respective pyrazoline precursors can be rationalized by the mechanism depicted in Scheme IV. On thermolysis, Δ^2-pyrazoline **7** loses nitrogen, probably via its tautomer[21] **6**, to generate (singlet) biradical **13**; compound **9** decom-

(18) A. L. Spek, *Cryst. Struct. Commun.*, **7**, 303 (1978).
(19) M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 937 (1972); M. Martin and M. Regitz, *Justus Liebigs Ann. Chem.*, 1702 (1974).
(20) R. M. Kellogg in "Photochemistry of Heterocyclic Compounds", Buchardt, Ed., Wiley, New York, 1976, Chapter 6.
(21) H. Meier and K. P. Zeller, *Angew. Chem.*, **89**, 876 (1977).
(22) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **101**, 4688 (1979).
(23) Curt Wentrup, "Reaktive Zwischenstufen", Vol. I, Georg Thieme Verlag, Stuttgart, 1979, Chapter 3.
(24) P. S. Engel, R. A. Hayes, L. Keifer, S. Szilagyi, and J. W. Timberlake, *J. Am. Chem. Soc.* **100**, 1876 (1978).

Scheme V



Scheme VI



poses (thermally or photochemically) to generate (singlet) biradical **15** (either by concerted or nonconcerted loss of nitrogen[24]). Biradicals **13** and **15** display ring closure to furnish cyclopropane derivatives **14** and **16**, respectively. Hence it appears that in this particular case the ring-closure process of **13** and **15** competes successfully with a rearrangement of the bicyclobutylcarbinyl biradicals, which contrasts with the results obtained in another type of reaction in which the analogous bicyclobutylcarbinyl monoradicals were shown[8] to display a fast homoallylic rearrangement, **18** → **19**, as represented in Scheme V.

This difference can be explained by regarding these singlet biradicals[23] either as transition states or as very short-lived species.[25] Also in related reactions involving intermediate bicyclobutylcarbinyl biradicals ring closure took place without rearrangement.[27] It appears that the process **9** → **16** occurs with complete retention of configuration in both the photochemical and thermal routes. Photolytically induced extrusions of nitrogen from pyrazolines to cyclopropanes are generally attended by a high degree of retention of configuration.[20] On the other hand, in some thermal extrusions, viz., on thermolyses of Δ^1-*trans*-3,5-alkylpyrazolines, predominant single inversion has been observed.[28] In the case of **9**, single inversion during the thermal reaction would have produced the cis isomer of **16** which is, however, expected to be strongly disfavored for steric and electronic reasons.

During the thermolysis of **9**, affording **16**, slow formation of dihydrobenzofuran **17** was observed. Compound **17** could be obtained in nearly quantitative yield by thermal decomposition of **16** in refluxing xylene solution. In addition to a concerted mechanism, stepwise pathways can account for the rearrangement **16** → **17** (Scheme VI): either via a cyclopropyl ketone–dihydrofuran rearrangement leading to benzvalene **20**, followed by valence isomerization of the bicyclobutane ring system to yield **17**, or the other way around via the intermediacy of cyclohexadienone **21**. Whatever the precise mechanism may be, the driving force of the rearrangement **16** → **17** is provided by the aromatization and relief of the steric crowding in **16**. In this context it is of interest to note that under the same conditions compounds **14** did not show such a thermally induced cyclopropyl ketone–dihydrofuran rearrangement.

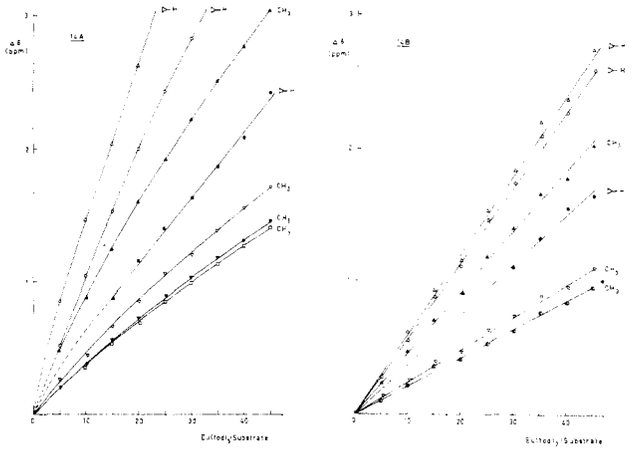


Figure 2. Plots of the observed shift enhancements ($\Delta\delta$) against the ratio Eu(fod)$_3$/substrate for compounds **14A and 14B** (*CH_3 indicates the case where the slopes of two lines coincide).

Cyclopropyl ketone–dihydrofuran rearrangements are not without precedent.[29-31] A phenyl-substituted cyclopropyl ketone has been shown to isomerize in high yield to the corresponding dihydrofuran in the melt.[31c] Related to the overall process **9** → **17** is the thermal decomposition of some α-ketopyrazolines, resulting in the formation of mixtures of cyclopropyl ketones and dihydrofurans, the latter probably arising from the former.[21,32] Mechanistic studies of the cyclopropyl ketone to dihydrofuran rearrangement have to our knowledge not yet appeared.

Structural Assignment of 14A and 14B. On the basis of only the ^{1}H NMR and ^{13}C NMR data it was not possible to assign structures **14A** and **14B** to the isomeric compounds obtained.[33] However, the results of Eu(fod)$_3$-induced[34] shift experiments have made it probable that the compound with a melting point of 78.8–80.3 °C possesses structure **14A** and that with a melting point of 99.0–100.0 °C structure **14B**. The ^{1}H NMR (downfield) induced shift enhancements of the absorptions of the isomers are shown as a function of the ratio Eu(fod)$_3$/substrate in Figure 2. On addition of increasing amounts of Eu(fod)$_3$, the initially overlapping absorptions due to the cyclopropyl hydrogen atoms are observed separately as apparent double doublets; due to line broadening no accurate values of the coupling constants could be derived, however.[33] A comparison of the plots obtained for isomers **14A** and **14B** shows that in the case of **14A** the shift enhancements of most signals,

(25) It is noteworthy that irradiation of compound **9** in benzene or acetone (which are sensitizers capable of energy transfer to pyrazolines)[26] afforded **16** as the only product.

(26) C. Gousetis and J. Sauer, *Tetrahedron Lett.*, 1295 (1979).

(27) M. Christl and H. Leininger, *Tetrahedron Lett.*, 1553 (1979).

(28) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).

(29) C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947); D. M. Aten Armitage and C. L. Wilson, *ibid.*, **81**, 2437 (1959).

(30) (a) B. M. Trost and P. L. Kinson, *Tetrahedron Lett.*, 2675 (1973); (b) *J. Am. Chem. Soc.*, **97**, 2438 (1975).

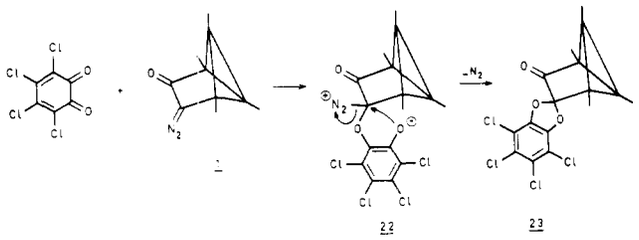
(31) (a) M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965); (b) S. J. Rhoads and R. D. Cockroft, *J. Am. Chem. Soc.*, **91**, 2815 (1969); (c) D. W. Boykin and R. E. Lutz, *ibid.*, **86**, 5046 (1964).

(32) R. Danion-Bougot and R. Carrié, *Bull. Soc. Chim. Fr.*, 3521 (1972).

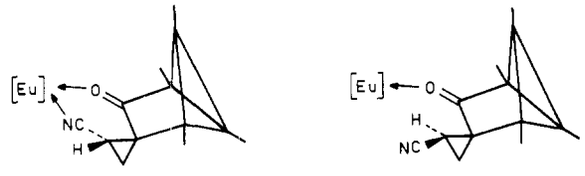
(33) An analogous problem has been solved by a comparison of IR and NMR data. O. Tsuge, I. Shinkai, and M. Koga, *J. Org. Chem.*, **36**, 745 (1971).

(34) Eu(fod)$_3$ = tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium.

Scheme VII



especially those due to the cyclopropyl hydrogen atoms, are more strongly dependent on the ratio Eu(fod)$_3$/substrate than those in the case of **14B**. For both **14A** and **14B** it may be assumed, on basis of literature data,[35] that Eu(fod)$_3$ will have a greater preference for coordination to the ketone rather than to the cyano group. However, in **14A** the cyano substituent is in the vicinity of the ketone function, so that Eu(fod)$_3$ can form a bidentate[36] complex,

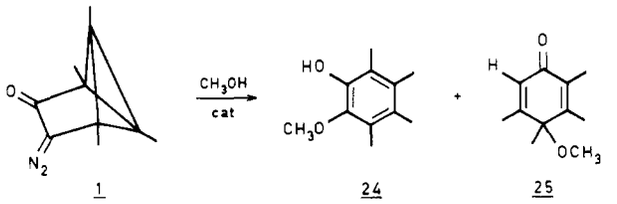


with both the ketone and cyano groups acting as ligands. Such a bidentate complex is not possible in the case of **14B**. This bidentate effect will favor complex formation, consequently giving rise to generally larger shift enhancements for **14A** as compared to those for **14B**.

Reaction with Tetrachloro-*o*-quinone. On treatment of diazo ketone **1** with 1 equiv of tetrachloro-*o*-quinone in CH_2Cl_2 solution at ambient temperature, instantaneous evolution of nitrogen occurred. After the workup an adduct could be isolated in 73% yield which was characterized as compound **23**. Although analogous fast reactions of diazoalkanes with quinones have been observed,[37,38] a number of α-diazo ketones, however, have proved to be unreactive toward tetrachloro-*o*-quinone[38] at ambient temperature. The reaction between tetrachloro-*o*-quinone and **1** is believed to involve the unstable zwitterionic intermediate **22**, which will afford **23** upon intramolecular S_N2 displacement of nitrogen by the phenolate anion[38] (Scheme VII). This mechanism explains elegantly why the bicyclobutane system remains intact; an alternative, less likely mechanism involves as the first step loss of nitrogen from **1**, to produce the corresponding α-keto carbene[37] which is prone to intramolecular rearrangement rather than to cycloaddition (see below).

Transition-Metal-Catalyzed Decompositions. The photolytic, thermal, and catalytic decomposition of α-diazo ketones is often accompanied by the well-known Wolff rearrangement[2a-c,3,4] in which α-keto carbenes and ketenes are generally believed to be intermediates. In the case of cyclic diazo ketones the Wolff rearrangement leads to ring contraction; this has found application for the preparation of certain strained-ring systems.[3g,30] Several attempts were made to accomplish a ring contraction of diazo ketone **1** either photochemically, thermally, or catalytically (transition metal) in various solvents. However, the photolytic decomposition in methanol and benzene furnished complicated mixtures of products in low yield which were not isolated. Hence, **1** fails to undergo a Wolff rearrangement, although it possesses the required cis geometry assumed to be necessary for α-diazo ketones to display ring contraction.[40] Probably the rearrangement of diazo ketone **1** would involve too great an increase in strain energy to allow for a feasible ring contraction.[30,41] Also, attempts to trap the intermediate α-keto carbene upon photolysis of **1** (with and without sensitizer) in the presence of the electron-rich alkene 2,3-dimethyl-2-butene were unsuccessful.[42]

Table I. Catalyzed Decomposition of 1 in Methanol

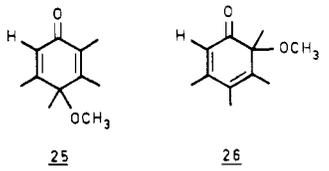


catalyst	ratio of catal/1	T, °C	t, h	yield,[a] % 24	25
$AgClO_4$[b]	0.1	−70 to 0[c]	18	30	44
$Cu(Acac)_2$	0.08	room temp	1.5	45[a]	
$Ru_2(OAc)_4$	0.005	−70 to 0[c]	18	30	13
none		room temp	30	21	16

[a] Yields were determined by integration of ^1H NMR spectra except for the $Cu(Acac)_2$ catalyst decomposition (yield of isolated product). [b] $AgClO_4$ was used in combination with 10 equiv of Na_2CO_3 (see text). [c] Reagents were mixed at −70 °C and subsequently warmed to 0 °C overnight (see Experimental Section).

Diazo ketones also decompose in the presence of transition-metal systems,[2a,5] e.g., silver salts, copper, copper derivatives, rhodium and palladium acetates, and tungsten hexachloride. When these decompositions are performed in the presence of suitable trapping agents, carbenoid addition products can be formed. The cyclopropanation reaction by copper catalysis has recently been reviewed.[2a] The exact nature of the intermediates is not known, but transient transition-metal carbene complexes[43,44] rather than free carbenes are assumed to be involved.

Catalyzed Decompositions in Methanol. The transition-metal-catalyzed decomposition of **1** was carried out in methanol with various catalysts; the results are compiled in Table I. The reactions gave, in most cases, complicated mixtures from which the two major products phenol **24** and 2,5-cyclohexadienone **25** could be isolated. The UV



(35) J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.*, **93**, 641 (1971).
(36) A number of 3-methoxy-substituted cycloalkanones, possessing a ketone and methoxy function in a suitable arrangement, have been shown to form such bidentate complexes with Eu(fod)$_3$. E. Dunkelblum and H. Hart, *J. Org. Chem.*, **42**, 3958 (1977).
(37) W. Ried and W. Radt, *Justus Liebigs Ann. Chem.*, **688**, 170 (1965).
(38) L. Horner and E. Lingnau, *Justus Liegbigs Ann. Chem.*, **573**, 30 (1951).
(39) L. Horner and E. Spietschka, *Chem. Ber.*, **88**, 934 (1955).
(40) F. Kaplan and M. L. Mitchell, *Tetrahedron Lett.*, 759 (1979).
(41) F. T. Bond and C. Y. Ho, *J. Org. Chem.*, **41**, 1421 (1976).
(42) Certain cyclopropyl carbenes were also shown to undergo fragmentation rather than addition: M. Oda, Y. Ito, and Y. Kitahara, *Tetrahedron Lett.*, 2587 (1975); *ibid.*, 977 (1978); W. R. Dolbier, O. T. Garza, and B. H. Al-Sader, *J. Am. Chem. Soc.*, **97**, 5038 (1975).
(43) W. R. Moser, *J. Am. Chem. Soc.*, **91**, 1135, 1141 (1969).
(44) Certain transition-metal complexes give stable metal carbene complexes upon treatment with diazo ketones. W. A. Herrmann, *Angew. Chem.*, **90**, 855 (1978).

Scheme X

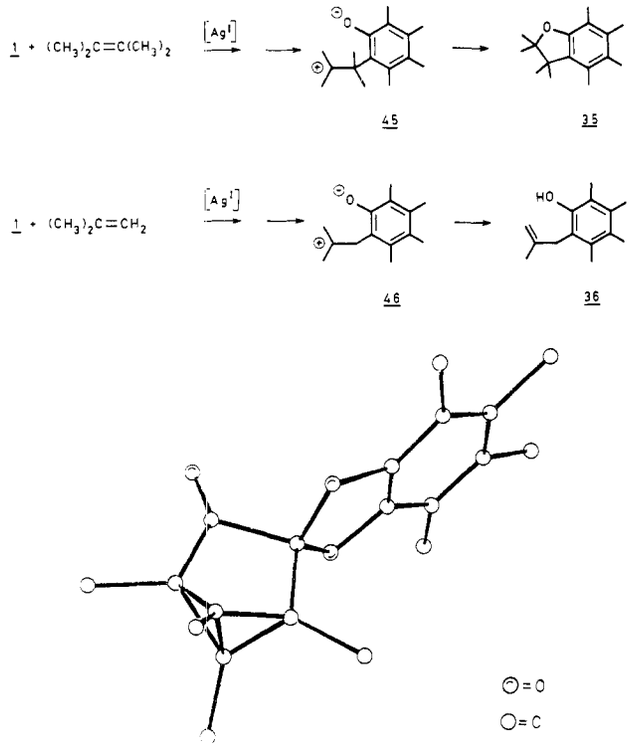


Figure 3. Structure of compound 47.

the model compound 40 proved to be stable under the reaction conditions. We cannot rule out rigorously the intermediacy of 41 as a short-lived intermediate, arising from direct addition of 38 to vinyl acetate, because of the facile rearrangement of such cyclopropyl ketones to dihydrofurans.[53] The observed orientation in the addition product 34 is in agreement with the occurrence in route ii of the zwitterionic intermediate 44.

The addition of 1 to 2,3-dimethyl-2-butene to provide dihydrobenzofuran 35 pursues the same course as shown for vinyl acetate; in the case of 2-methylpropene, however, no dihydrobenzofuran but instead phenol 36 was obtained. This difference in behavior must arise from subtle differences in activation energies of the two reaction pathways that are open for intermediate zwitterions 45 and 46 and/or in thermodynamic stabilities[54] of the reaction products 35 and 36, respectively (Scheme X).

Rhodium-Catalyzed Decomposition. Treatment of diazo ketone 1 in 2,3-dimethyl-2-butene (or pentane) solution with a catalytic amount (0.5 mol %) of rhodium acetate at −80 °C followed by warming of the mixture to 0 °C afforded a complicated reaction mixture. However, none of 35, arising from a 1,3-dipolar addition of the corresponding keto carbene to the alkene, could be detected. A crystalline product, 47, was obtained in 15% yield on the application of preparative TLC to this reaction mixture; its structure (shown in Figure 3) was determined unequivocally by Mr. F. van Bolhuis using X-ray techniques.[55]

Compound 47 can be regarded formally as being formed by dimerization of the α-keto carbene, originating from 1

Scheme XI

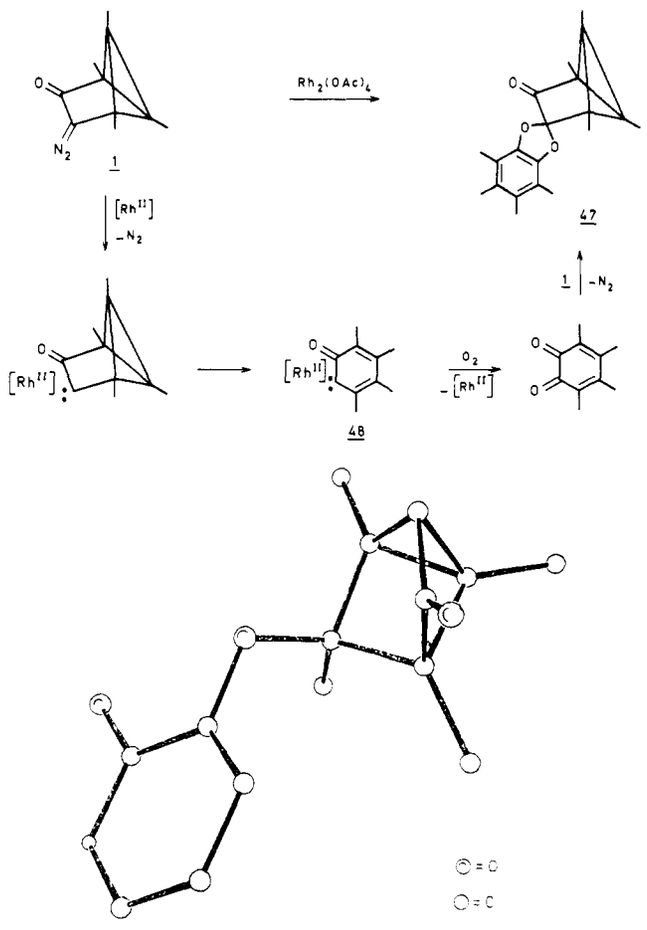


Figure 4. Structure of compound 49.

with incorporation of an oxygen atom. Although the origin of the oxygen atom has not been established, molecular oxygen might well be the source. The formation of 47 can be interpreted by the mechanism represented in Scheme XI, which involves oxidation of the rhodium-coordinated carbene 48 to tetramethyl-*o*-quinone. The intermediacy of tetramethyl-*o*-quinone is supported by the close analogy to the reaction of 1 with tetrachloro-*o*-quinone to give 23 (Scheme VIII). In this context it is noteworthy that certain carbenes have been shown to react with molecular oxygen to provide the corresponding ketones[2j,56] and, moreover, that certain rhodium complexes are catalysts in the deoxygenation of 1,6-dimethyloxepine to *o*-xylene.[57]

Reaction with *o*-Dihydroxybenzene. In view of the reaction of diazo ketone 1 with tetrachloro-*o*-quinone (Scheme VII) and the supposed intermediacy of tetramethyl-*o*-quinone in the formation of 47 (Scheme XI), it was of interest to study the reaction of 1 with *o*-dihydroxybenzene.

Treatment of 1 with excess *o*-dihydroxybenzene at −80 °C afforded after preparative TLC in 40% yield a mixture of two compounds, which was separated into its components (ratio 2:1) by applying high-pressure LC. The mass spectroscopic data indicated that both compounds were 1:1 adducts of *o*-dihydroxybenzene and 1 minus nitrogen. The detailed molecular structure could not be elucidated unambiguously with conventional spectroscopic techniques; therefore, an X-ray investigation was performed

(53) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **48**, 1297 (1965).

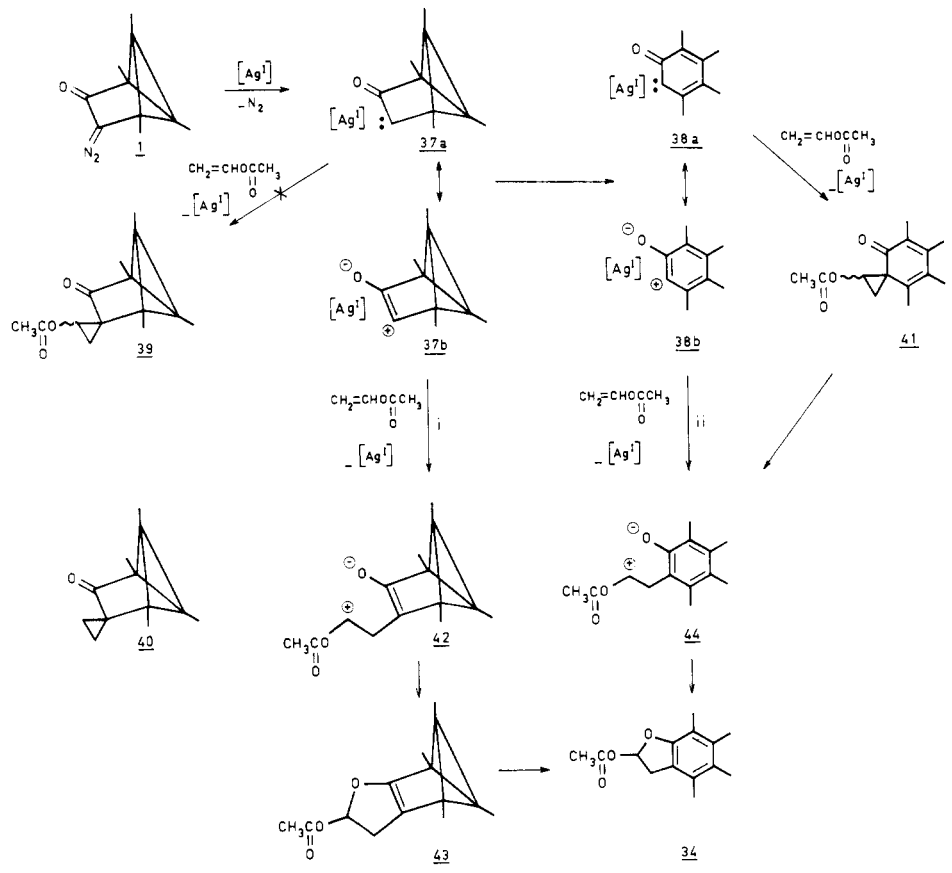
(54) Indeed, it has been shown that *o*-allylphenols, analogous to **36**, can be readily converted into the corresponding dihydrobenzofurans. E. Schmid, G. Frater, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 1625 (1972).

(55) F. van Bolhuis, to be submitted for publication.

(56) R. W. Murray and A. Suzui, *J. Am. Chem. Soc.*, **93**, 4963 (1971); *ibid.*, **95**, 3343 (1973).

(57) H. C. Volger, H. Hogeveen, and C. F. Roobeek, *Recl. Trav. Chim. Pays-Bas*, **92**, 1223 (1973).

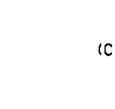
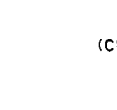
Scheme IX



rearrangement to dihydrofurans;[29-32] see Scheme VI) in the reaction with alkenes has not been definitely ruled out.[52a]

The silver perchlorate/sodium carbonate catalyzed decomposition of diazo ketone 1 in the presence of a large excess of certain electron-rich alkenes provided products that can be regarded as arising from a formal 1,3-dipolar addition of the corresponding α-keto carbenoid to the alkene accompanied by valence isomerization of the bicyclobutane moiety; the results are compiled in Table II. It should be noted that at ambient temperature in the absence of catalyst, diazo ketone 1 is unreactive toward the electron-rich alkenes employed, in contrast to its behavior toward electron-deficient alkenes; this renders the intermediacy of pyrazolines unlikely.

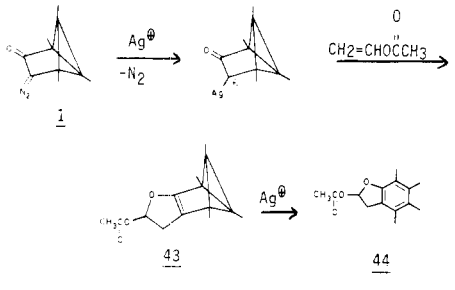
Table II. Silver-Catalyzed[a] Carbenoid Additions of Diazo Ketone 1 to Electron-Rich Alkenes[b]

alkene	product	yield,[c] %
$CH_2=CHOCCH_3$ (O)	 34	31
$(CH_3)_2C=C(CH_3)_2$	 35	71
$(CH_3)_2C=CH_2$	 36	59

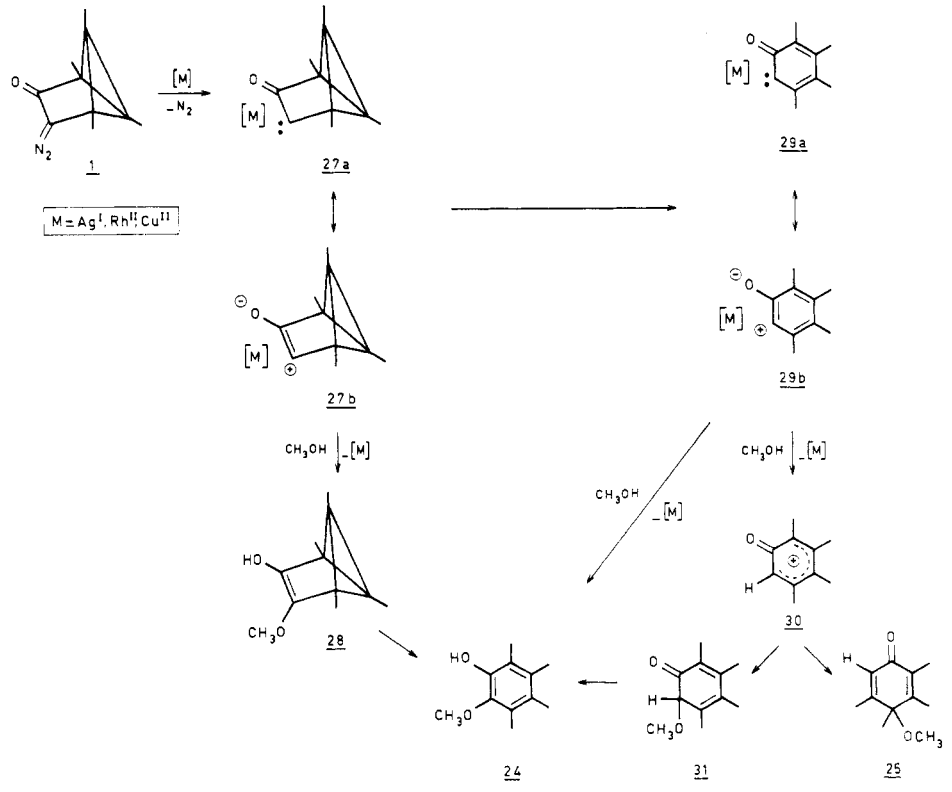
[a] Catalyst system $AgClO_4/Na_2CO_3$. Ratio of $AgClO_4/Na_2CO_3$/alkene of 1:10:10. [b] Reaction conditions: reagents were mixed at −70 °C and then warmed to 0 °C overnight. [c] Yields were determined by ^1H NMR spectroscopic integration.

A reasonable mechanism[52b] of these carbenoid additions is shown in Scheme IX, as exemplified for vinyl acetate. The formation of **34** can be accounted for in principle by the "benzvalene" route (i) via **43** or by the "aromatic" route (ii) via **38**: the latter is favored because in no case have products been obtained containing the benzvalene skeleton. Direct addition of **37** to vinyl acetate would produce **39** which might isomerize to dihydrobenzfuran **34**: this possibility was shown to be very unlikely, however, because

(52) (a) For instance, in the (formal) 1,3-dipolar addition of ethyl diazoacetate to alkynes to afford furans it has been shown that the furans result from rearrangement of the initially formed cyclopropene derivatives.[2d] I. A. Dyakonov, M. I. Komendatov, and T. S. Smirnova, *Zh. Org. Khim.*, **5**, 1742 (1969). (b) A referee has suggested the intermediacy of an argentocarbonium ion in the silver-catalyzed addition of diazo ketone 1 to electron-rich alkenes (and similar carbonium ions in the other transition-metal-catalyzed reactions). However, the occurrence of an α-keto carbonium ion in this system would probably have led to different reaction products as shown in the conversion of **1** to **49** and **51**, involving ion **53** as an intermediate (Scheme XII). On this basis a formulation of the transition-metal-catalyzed reactions of **1** via a complexed carbene is preferred (Schemes VIII, IX, and XI).



Scheme VIII

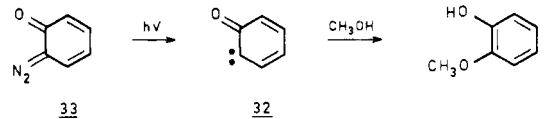


spectrum of **25** shows a maximum at λ 230 nm (ε 9200), quite similar to that of the reported 4-hydroxy-2,4,6-trimethyl-2,5-cyclohexadienone[45] [λ_{max} 232 nm (ε 13560)]; this excludes the isomeric structure **26** which would exhibit a UV absorption maximum at about 310 nm (compare 6-hydroxy-2,4,6-trimethyl-2,4-cyclohexadienone[45]).

The overall yield as well as the product ratio for **24**/**25** proved to be dependent on the catalyst used[46] (see Table I). Silver perchlorate was used in combination with an excess of sodium carbonate to prevent possible acid-catalyzed reactions; this system[47] has recently been applied for the valence isomerization of substituted benzvalenes.[49] Both compounds **24** and **25** were also obtained when **1** was left in methanol solution without catalyst (Table I), but in this case the rate of the decomposition was low, **1** still being present after 18 h at room temperature.

A conceivable mechanism to account for the formation of **24** and **25** is depicted in Scheme VIII. In the first step of the process the metal removes nitrogen from **1** to provide transient metal-coordinated carbene **27**. α-Keto carbenes are attributed an appreciable participation from the dipolar canonical form:

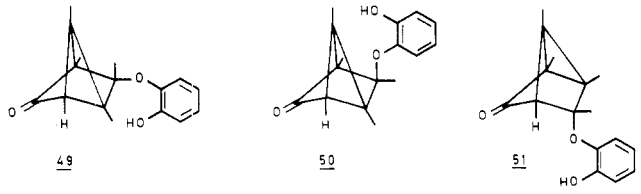
Therefore, we can consider for the metal-coordinated carbene **27** two resonance structures, **27a** and **27b**. In principle, solvolysis of **27** by methanol might give rise to formation of benzvalene **28** which would display valence isomerization (possibly transition-metal catalyzed)[49] to afford phenol **24**. This reaction path, however, does not explain the formation of **25**; moreover, the strained carbenoid **27** is expected to be very prone to rearrangement. Therefore, it is reasonable to assume that **27** rearranges to **29** before being quenched by the solvent. Carbenoid **29** either may be solvolyzed directly to provide **24** or may abstract a proton from methanol to give carbocation **30** which can afford **25** and **31** upon reaction with methanol, compound **31** being rapidly tautomerized to **24**. The proposed intermediacy of carbenoid **29** in the formation of **24** and **25** is in agreement with the reported finding that the related free carbene **32**, which was generated by photolysis of diazo ketone **33** in methanol solution, was shown to give as major product 2-methoxyphenol.[50]



Carbenoid Additions to Electron-Rich Alkenes. The formal 1,3-dipolar addition of α-keto carbenes is well established by the reaction with various unsaturated substrates such as alkenes, alkynes, nitriles, carbon disulfide, and isothiocyanates to afford five-membered heterocyclics.[51] Although the observed regiospecificity is in agreement with the proposed 1,3-dipolar character of these additions, the detailed reaction path has not unequivocally been proved: the possible intermediacy of, for instance, pyrazolines or cyclopropyl ketones (the latter capable of

(45) J. Derkosch and W. Kaltenegger, *Monatsh. Chem.*, **88**, 778 (1957).
(46) Transition-metal-catalyzed decompositions of diazo derivatives in methanol have also in other cases been shown to depend on the particular catalyst. R. V. Hoffman and H. Shechter, *J. Am. Chem. Soc.*, **100**, 7934 (1978).
(47) The exact nature of the catalyst is unknown. When a benzene solution of $AgClO_4$ was stirred with Na_2CO_3, it was shown that silver had completely precipitated, probably as Ag_2CO_3.[48] Therefore in the $AgClO_4/Na_2CO_3$-catalyzed reactions, heterogeneous catalysis by Ag_2CO_3 rather than homogeneous catalysis by $AgClO_4$ may occur. Whereas diazo ketone **1** is readily decomposed with the catalyst system, certain other diazo ketones (diazocamphor, diazoquinone) proved to be stable.
(48) B. J. Nusse, Thesis, The University, Groningen, 1978, p 90.
(49) H. Hogeveen and W. F. J. Huurdeman, *J. Am. Chem. Soc.*, **100**, 860 (1978).
(50) M. Yagihara, Y. Kitahara, and T. Asao, *Chem. Lett.*, 1015 (1974).
(51) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); R. Huisgen, G. Binsch, and H. König, *Chem. Ber.*, **97**, 2868, 2884, 2893 (1964).

by Mr. F. van Bolhuis for the major compound **49**, and the



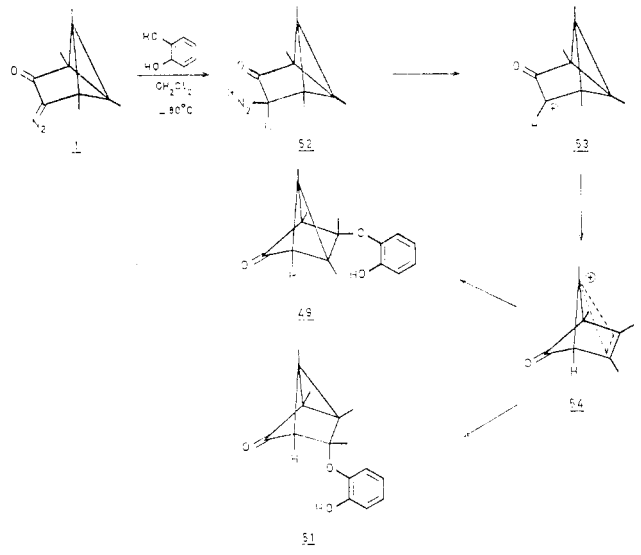
structure is shown in Figure 4.[58] The general similarities between the spectroscopic data (see Experimental Section) of the adducts suggest that both compounds possess the tricyclo[2.2.0.0^{2,6}]hexane carbon skeleton. The minor compound is believed to have structure **51** rather than **50** for the following reasons. (i) The singlet due to the ring-hydrogen atom is found at δ 2.52 in **49** and at δ 3.11 in **51** ($CDCl_3$ solution); a smaller difference would have been expected in case of geometric isomers **49** and **50**. (ii) The ^{13}C NMR spectrum of **49** shows the absorptions due to the skeletal tertiary carbon atom at δ 50.6 (J_{CH} = 180 Hz) whereas the corresponding signal of **51** is observed at δ 67.1 (J_{CH} = 168 Hz). J_{CH} is known to be dependent on the ring strain;[59] its smaller value for the skeletal tertiary carbon atom in the case of **51** strongly suggests that the carbon atom is at a less strained position of the ring system than that in **49**, where it is situated at the bridgehead of a three- and a four-membered ring. The position of the phenol moiety in **51** is likely to be endo on basis of the mechanism of formation (Scheme XII). This mechanism involves the bicyclobutylcarbinyl cation **53**, generated by loss of nitrogen from the initially formed diazonium ion **52**. Bicyclobutylcarbinyl cation **53**, being a secondary carbonium ion and destablized by the α-ketone function, will readily undergo a 1,2 alkyl shift to furnish the nonclassical ion **54**. The reaction of such a nonclassical ion with nucleophiles is known to occur by backside attack on the three-center bond to yield endo-substituted products,[60] in agreement with the stereochemistry observed for **49** and assumed for **51**.

Experimental Section

General Procedures. All reagents and solvents were purified when necessary by standard methods. Elemental analyses were performed in the microanalytical department of this laboratory. Melting points were determined on a Mettler FP2 melting point apparatus equipped with a Mettler FP52 microscope. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Mass spectra were measured on an AEI MS-902 apparatus by Mr. A. Kiewiet. ^1H NMR spectra were determined with a Hitachi Perkin-Elmer R24B or a JEOL C-60 HL spectrometer with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded by using a Varian XL-100 spectrometer operating at 25.2 MHz. UV spectra were obtained with a Beckman DB-G spectrophotometer. Analytical and preparative-scale separations by means of high-pressure liquid chromatography were carried out with a Waters high-pressure LC ALC/GPC apparatus equipped with a differential and a Schoeffel Spectraflow SF 770 monitor. Separations by gas–liquid chromatography were carried out on a Hewlett-Packard F&M 700 apparatus equipped with a flame ionization detector. Irradiations were performed with a Hanau Q-81 medium-pressure mercury arc, equipped with a Pyrex filter.

Synthesis of Tosylhydrazone 3. To 246 mg (1.5 mmol) of diketone **2** in 5 mL of CH_2Cl_2 was added dropwise 280 mg (1.5 mmol) of tosylhydrazine in 10 mL of CH_2Cl_2. The solution was

Scheme XII



stirred at room temperature for 15 min. Evaporation of solvent in vacuo and crystallization from CCl_4 afforded 398 mg (1.2 mmol, 80% yield) of **3** as white crystals: mp 125–130 °C dec; IR (KBr pellet) 3230 (NH), 1705 (C=O), 1635 (C=N), 1350 and 1165 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.17 (s, 3 H), 1.53 (s, 6 H), 2.40 (s, 3 H), 7.28/7.80 (AB q, J = 13 Hz), 11.46 (s, intramolecularly bonded NH); ^{13}C NMR ($CDCl_3$) δ 3.3 (q), 3.9 (q), 5.7 (q), 21.4 (q), 33.2, 41.7, 51.4, 127.5 (d, J_{CH} = 165 Hz), 129.4 (d, J_{CH} = 160 Hz), 135.6, 143.7, 151.8 (C=N), 204.5 (C=O); mass spectrum, m/e 177 (M^+ – Tos), 149 ($M^+ - N_2$ – Tos). Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61,41; H, 6.06; N, 8.43; S, 9.65. Found: C, 61.27; H, 6.18; N, 8.41; S, 9.57.

Synthesis of Bis(tosylhydrazone) 4. A 164-mg sample (1.0 mmol) of diketone **2** and 372 mg (2.0 mmol) of tosylhydrazine were stirred in 10 mL of methanol at 40 °C for 1 h. Evaporation of the solvent and recrystallization of the residue from methanol afforded 300 mg (0.6 mmol, 60% yield) of **4** as white crystals, mp 142.2–143 °C. Compound **4** was also obtained by treatment of **3** with 1 equiv of tosylhydrazine in methanol solution at 60 °C: IR (KBr pellet) 3200 (NH), 1610 (C=N), 1590 (arom), 1320 and 1160 (SO_2) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.00 (s, 3 H), 1.39 (s, 9 H),[61b] 2.39 (s, 3 H), 2.52 (s, 3 H), 8.00–7.20 (m, 8 H), 10.50 (s, 1 H, intermolecularly[61a] bonded NH), 11.50 (s, 1 H, intramolecularly[61a] bonded NH); ^{13}C NMR (Me_2SO-d_6) δ 2.7 (q), 5.5 (q), 9.0 (q), 20.9 (q), 21.0 (q), 34.3, 43.5, 45.5, 126.8 (d, J_{CH} = 165 Hz), 128.1 (d, J_{CH} = 165 Hz), 129.6 (d, J_{CH} = 160 Hz), 129.8 (d, J_{CH} = 163 Hz), 134.3, 135.8, 143.8, 144.0, 154.0 (C=N), 165.7 (C=N); mass spectrum, m/e 472 ($M^+ - N_2$). Anal. Calcd for $C_{24}H_{28}N_4O_4S_2$: C, 57.58; H, 5.63; N, 11.19; S, 12.81. Found: C, 57.52; H, 5.63; N, 11.44; S, 12.80.

Attempted Preparation of Diazo Ketone 1 from Tosylhydrazone 3. (1) With Basic Alumina. To a solution of 190 mg (0.58 mmol) of **3** in 100 mL of CH_2Cl_2 and 100 mL of ether was added 70 mg of basic alumina (activity I). After the mixture was stirred for 2 h and filtered and the solvent evaporated, compound **3** was recovered unchanged (according to ^1H NMR spectroscopy). The same result was obtained when **3** was chromatographed on a basic alumina (activity I) column (eluent CH_2Cl_2).

(2) With Aqueous NaOH Solution. To a solution of 110 mg (0.30 mmol) of **3** in 10 mL of hexane and 30 mL of ether was added 50 mL of a 0.1 N NaOH solution. The two-phase system was vigorously stirred for 2 h. The two layers were separated, the organic layer was collected, washed with water, and dried over

(58) F. van Bolhuis, to be submitted for publication.
(59) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 334.
(60) H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **95**, 7315 (1973).

(61) (a) When a small amount of water was added to a Me_2SO-d_6 solution of **3**, line broadening of the NH signal at δ 10.50 and the H_2O signal at δ 3.30 occurred upon warming to 65 °C, whereas the NH absorptions at δ 11.50 remained sharp. From this we conclude that the signal at δ 10.50 is due to an intermolecularly bonded NH proton and the signal at δ 11.50 to the more tightly intramolecularly bonded NH proton. (b) This absorption is split into two peaks at δ 1.40 (s, 6 H) and 1.43 (s, 3 H) in $CDCl_3$ solution.

Na_2SO_4, and the volatile material was evaporated, leaving a complicated mixture (according to ^1H NMR spectroscopy) which was not separated.

Synthesis of Hydrazone 5. A solution of 50 μL of hydrazine hydrate in 10 mL of methanol was added to a solution of 167 mg (1.0 mmol) of diketone **2** in 10 mL of methanol. The reaction mixture was boiled for 1.5 h. Evaporation of the solvent afforded 180 mg of a yellow oil containing hydrazone **5** in about 90% yield (based on ^1H NMR spectroscopic integration). No further purification could be achieved. Spectroscopic data for **5**: IR (neat) 3420 (NH), 1700 (C=O), 1600 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.23 (s, 3 H), 1.59 (s, 6 H), 7.18 (br, 2 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 2.9 (q), 3.5 (q), 5.6 (q), 33.4, 40.5, 50.6, 144.9 (C=N), 196.2 (C=O); mass spectrum, found *m/e* 178.111, calcd *m/e* 178.113 (M^+).

Synthesis of 4-Diazo-1,2,5,6-tetramethyltricyclo-[3.1.0.0^{2,6}]hexan-3-one (1). To a solution of 180 mg of crude hydrazone **5** (see above) in 10 mL of CH_2Cl_2 was added 1 g of Na_2SO_4 and 300 mg of freshly activated MnO_2 (see note below) in 2 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at room temperature, subsequently 150 mg of MnO_2 in 2 mL of CH_2Cl_2 was introduced, and the mixture was again stirred for 1 h at room temperature. After filtration over Celite and evaporation of the solvent, about 170 mg of an orange oil was obtained that contained, according to a ^1H NMR integration, 60–80% diazo ketone (the yield, based on intake of diketone **2**, varied, depending on the quality of MnO_2). Diazo ketone **1** is thermally unstable above 10 °C; but when stored at −20 °C in solution, it is fairly stable for several days. Attempts to purify **1** by preparative TLC and high-pressure LC resulted in decomposition; therefore, **1** was used without further purification. In each experiment **1** was freshly prepared from diketone **2** according to the procedure described above. The amount of **1** was determined by ^1H NMR spectroscopic integration of the sample used.

Activated MnO_2 was prepared according to the procedure of Attenburrow et al.[62] The quality of the MnO_2 used proved to be critical in order to obtain a good yield of **1**. The best results were obtained when the wet MnO_2 cake was partially dried at 50 °C in vacuo (until it contained 20–30% moisture), stored as such, and activated for every experiment by being dried for 16–20 h at 50 °C in vacuo with P_2O_5 as the drying agent. Spectroscopic data of **1**: IR (neat) 2060 (N=N), 1690 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.32 (s, 3 H), 1.47 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 2.8 (q), 4.8 (q), 7.3 (q), 25.8, 37.2, 37.4, 51.2 (C=N),[63] 196.6 (C=O); mass spectrum, found *m/e* 148.089, calcd *m/e* 148.090 ($M^+ - N_2$).

Reaction of 1 with Acrylonitrile. Synthesis of Δ^2-Pyrazoline 7. To a solution containing 0.78 mmol of **1** in CH_2Cl_2 was added 1 mL of acrylonitrile. The reaction mixture was boiled for 15 min, followed by evaporation of the solvent in vacuo, leaving 230 mg of **7** as a brown oil containing **7** in 92% yield (determined by ^1H NMR spectroscopic integration). The attempted purification of **7** by chromatography and crystallization was unsuccessful: IR (neat) 3290 (NH), 2210 (C≡N), 1720 (C=O), 1525 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 3 H), 1.12 (s, 3 H), 1.48 (s, 3 H), 1.52 (s, 3 H), 2.76–2.92 (Ab system, J = 17 Hz, 2 H), 6.85 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 2.3 (q), 2.8 (q), 4.2 (q), 5.3 (q), 24.0, 26.8, 37.9 (t, J_{CH} = 138 Hz), 42.8, 51.9, 73.1, 114.3 (C≡N), 119.5 and 210.5 (C=O); mass spectrum, found *m/e* 229.126, calcd *m/e* 229.122 (M^+).

Observation of Δ^1-Pyrazoline 6. A solution containing 0.60 mmol of **1** in 0.5 mL of $CDCl_3$ was introduced into an NMR tube. The solution was frozen at liquid nitrogen temperature. Subsequently 0.1 mL of $CDCl_3$ was introduced and also frozen, followed by the addition of 70 μL (1 mmol) of acrylonitrile. The mixture was warmed to −70 °C, after melting, the layers were mixed with a glass rod, and ^1H NMR spectra were recorded from −70 to 30 °C at intervals of 10 °C. The NMR data obtained are cited in the text.

Reaction of 1 with Enone 8. Synthesis of Pyrazoline 9. To a solution containing 0.82 mmol of **1** in CH_2Cl_2 was added 162 mg (1.0 mmol) of enone **8** in 2 mL of CH_2Cl_2. The reaction mixture was stirred for 17 h at room temperature, followed by evaporation of the solvent, leaving 185 mg of a yellow-brown crystalline residue. Crystallization from methanol at −20 °C afforded 270 mg (0.68 mmol, 85% yield) of **9** as white crystals: mp 140–145 °C dec (N_2 evolution); IR (KBr) 1720 (C=O) cm^{-1}; UV (ethanol) λ_{max} 214 nm (ε 6300), 253 (3700), 318 (1000); ^1H NMR ($CDCl_3$) δ 1.05 (s, 6 H), 1.18 (s, 6 H), 1.35 (s, 2 H), 1.47 (s, 6 H), 1.65 (s, 6 H); ^{13}C NMR δ 2.5 (q), 3.2 (q), 4.3 (q), 6.1 (q), 26.0 (t, J_{CH} = 134 Hz), 26.2, 28.6, 42.5, 52.5, 102.3 (C-N), 211.7; mass spectrum, *m/e* 310 ($M^+ - N_2$). Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.51; H, 7.74; N, 8.28. Found: C, 74.11; H, 7.75; N, 8.50.

Reaction of 1 with Dimethyl Acetylenedicarboxylate. Synthesis of Pyrazole 11. A solution of 284 mg (2.0 mmol) of dimethyl acetylenedicarboxylate in 5 mL of CH_2Cl_2 was added to 1.3 mmol of **1**. The reaction mixture was allowed to stand for 17 h at room temperature. Subsequently the solvent and excess dimethyl acetylenedicarboxylate were removed in vacuo, leaving a crystalline solid, which was crystallized from CCl_4 at −20 °C to afford 230 mg (0.72 mmol, yield 57%) of **11** as colorless crystals: mp 140.5–141.3 °C; IR (KBr) 1730 (C=O), 1570 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 3 H), 1.42 (s, 3 H), 1.60 (s, 6 H), 3.90 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 4.2 (q), 9.1 (q), 10.9 (q), 38.8, 44.0, 46.9, 51.9 (q), 52.1 (q), 114.6, 144.0, 147.8, 160.9 (C=O), 163.3 (C=O), 167.5 (C=O); mass spectrum, *m/e* 318 (M^+). Anal. Calcd for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.03; H, 5.63; N, 8.91.

Thermolysis of Pyrazoline 7. Synthesis of 14A and 14B. A solution of 825 mg (3.6 mmol) of **7** in 5 mL of xylene was boiled for 9 h. Removal of the solvent in vacuo left a solid residue consisting of a mixture of isomers **14A** and **14B**. This mixture was separated into its components by applying high-pressure LC (silica gel, CH_2Cl_2/hexane 82/18), affording consecutively 280 mg (1.4 mmol, 34%) of **14A** and 250 mg (1.2 mmol, 30%) of **14B**. Crystallization from methanol at −40 °C and from hexane afforded isomer **14A** as white crystals: mp 78.8–80.3 °C; IR (neat) 2225 (C≡N), 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.22 (s, 3 H), 1.52 (s, 3 H), 1.57 (s, 3 H), 1.12–1.57 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 2.5 (q), 3.0 (q), 4.5 (q), 6.6 (q), 6.6 (d, J_{CH} = 174 Hz), 13.9 (t, J_{CH} = 165 Hz), 29.9, 30.2, 36.4, 36.7, 52.1, 119.5 (C≡N), 212.3 (C=O); mass spectrum, found *m/e* 201.116, calcd *m/e* 201.115 (M^+). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.56; H, 7.51; N, 6.96. Found: C, 77.49; H, 7.46; N, 6.92.

Further purification of isomer **14B** was achieved by crystallization from hexane/CH_2Cl_2 and CCl_4 which afforded **14B** as white crystals: mp 99.0–100.0 °C; IR (neat) 2225 (C≡N), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.13 (s, 3 H), 1.48 (s, 3 H), 1.50 (s, 3 H), 0.88–1.66 (m, 3 H); ^{13}C NMR (CDC_3) δ 2.7 (q), 2.7 (q), 4.4 (q), 5.1 (d, J_{CH} = 174 Hz), 5.4 (q), 13.6 (t, J_{CH} = 162 Hz), 29.1, 29.6, 36.2, 36.8, 52.3, 117.7 (C≡N), 210.5 (C=O); mass spectrum, found *m/e* 201.116, calcd *m/e* 201.115 (M^+). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.56; H, 7.51; N, 6.96. Found: C, 77.49; H, 7.51; N, 6.93. The shift reagent experiments with **14A** and **14B** were performed by adding samples of 50 μL of a $CDCl_3$ solution of $Eu(fod)_3$ (0.3 mmol/mL) with a syringe to 0.4 mL of a $CDCl_3$ solution of the substrate (0.3 mmol). The ^1H NMR spectra were recorded after each addition of $Eu(fod)_3$.

Photolysis of Pyrazoline 9. Synthesis of Bis(bicyclobutyl ketone)-Substituted Cyclopropane 16. A solution of 2.00 g (5.90 mmol) of pyrazoline **9** in 1 L of CH_2Cl_2 was irradiated in portions of 50 mL; each portion was irradiated until the evolution of nitrogen stopped (about 5 min). The solvent was removed in vacuo, leaving a solid that was crystallized from methanol and from hexane to afford 945 mg (3.10 mmol, 53% yield) of **16** as slightly yellow crystals: mp 107.2–109.2 °C; IR (CCl_4) 1710 (C=O) cm^{-1}; UV (ethanol) λ_{max} 216 nm (ε 4200), 240 (3000), 295 (290); ^1H NMR ($CDCl_3$) δ 1.07 (s, 12 H), 1.37 (s, 2 H), 1.39 (s, 6 H), 1.43 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 2.2 (q), 2.8 (q), 4.5 (q), 9.5 (q), 14.5 (t, J_{CH} = 162 Hz), 28.3, 31.8, 38.4, 41.3, 51.9, 213.9 (C=O); mass spectrum, found *m/e* 310.193, calcd *m/e* 310.195 (M^+).

Thermolysis of Pyrazoline 9. Synthesis of Dihydrobenzofuran 17. A solution of 80 mg (0.23 mmol) of pyrazoline **9** in 10 mL of xylene was boiled for 16 h. The solvent was removed in vacuo, leaving a yellow oil that soon started to crystallize. Crystallization from hexane afforded 30 mg (0.10 mmol, 44% yield) of dihydrobenzofuran **17** as white crystals, mp 149–158 °C.

(62) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
(63) Compare for ^{13}C NMR data of diazo ketones: T. A. Albright and W. J. Freeman, *Org. Magn. Reson.*, **9**, 75 (1977).

In a small-scale experiment, a solution of 20 mg of **9** in 0.5 mL of Me_2SO-d_6 kept in an NMR tube was heated at 120 °C. ^1H NMR spectra were run at intervals of 1 h, showing that after 7 h complete conversion of **9** into **16** and to a small extent **17** had occurred. When **16** was heated in *o*-dichlorobenzene solution at 140 °C for 16 h, complete conversion of **16** occurred to furnish **17** in nearly quantitative yield: IR (CCl_4) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 1.14 (s, 3 H), 1.47 (s, 3 H), 1.56 (s, 3 H), 2.08 (s, 12 H), 2.99 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 2.3 (q), 3.0 (q), 4.1 (q), 5.1 (q), 12.0 (q), 15.0 (q), 15.5 (q), 16.4 (q), 22.5, 27.0, 33.3 (t, J_{CH} = 132 Hz), 42.6, 47.9, 87.5, 114.5, 121.0, 126.1, 128.7, 134.3, 155.6, 214.0 (C=O); mass spectrum, *m/e* 310 (M^+). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.26; H, 8.44. Found: C, 81.04; H, 8.41.

Reaction of 1 with Tetrachloro-*o*-quinone. Synthesis of 23. To a stirred solution containing 0.62 mmol of **1** in 10 mL of CH_2Cl_2 was added 350 mg (1.24 mmol) of tetrachloro-*o*-quinone at room temperature. At once a vigorous evolution of nitrogen occurred. The solvent was removed in vacuo, leaving a black residue which was dissolved in 30 mL of boiling methanol with the help of a small amount of chloroform. When the mixture cooled to room temperature, 178 mg (0.45 mmol, 73% yield) of **23** was obtained as white crystals: mp 240.0–240.1 °C; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.23 (s, 3 H), 1.60 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 2.5 (q), 4.1 (q), 4.3 (q), 23.5, 39.2, 48.7, 112.2, 116.3, 125.0, 144.9, 203.0 (C=O); mass spectrum ($C_{16}H_{12}{}^{35}Cl_4O_3$), *m/e* 392 ($M^+$). Anal. Calcd for $C_{16}H_{12}Cl_4O_3$: C, 48.76; H, 3.07; Cl, 35.99. Found: C, 48.61; H, 3.07; Cl 36.22.

Direct Irradiations of 1. A deaerated solution containing 1.0 mmol of **1** in 150 mL of methanol was irradiated for 4 h at room temperature. The solvent was removed in vacuo, leaving a dark brown oil which did not contain starting material as shown by IR spectroscopy. According to GLC measurements, at least ten products were present in low yield which could not be separated by applying preparative TLC (silica gel, CH_2Cl_2).

Sensitized Irradiation of 1 in 2,3-Dimethyl-2-butene. A solution of 0.75 mmol of **1** and 138 mg (0.75 mmol) of benzophenone (sensitizer) in 10 mL of 2,3-dimethyl-2-butene was irradiated until **1** had completely decomposed according to IR spectroscopy. The solvent was removed in vacuo, leaving an orange residue consisting of several products. The residue was subjected to preparative TLC, but no products arising from **1** could be isolated.

$AgClO_4$-Catalyzed Decomposition of 1 in Methanol. Synthesis of 24 and 25. A solution containing 2.0 mmol of **1** in 10 mL of methanol was added dropwise to a stirred mixture of 63 mg (0.30 mmol) of silver perchlorate and 318 mg (3.0 mmol) of sodium carbonate in 30 mL of dry methanol while the temperature was maintained at −70 °C. Stirring was continued for 7 h at −70 °C, after which the mixture was allowed to warm to 0 °C overnight. Filtration over Celite and removal of the solvent in vacuo afforded 720 mg of a brown oil which contained **24** in 30% and **25** in 44% yield as determined by ^1H NMR spectroscopic integration. Separation of the mixture into its components was achieved by preparative TLC (silica gel, CH_2Cl_2) which furnished 60 mg (0.33 mmol, 16% yield) of **24** as a white solid (mp 68.5–69.5 °C after crystallization from hexane) and 120 mg of a yellow oil containing **25** in 19% yield as determined by ^1H NMR spectroscopic integration. Final purification of **25** was accomplished by repeated preparative TLC (alumina, benzene) to afford **25** as a slightly yellow oil. Spectroscopic data of **24**: IR (KBr) 3420 (OH) cm^{-1}; ^1H NMR (C_6D_6) δ 1.98 (s, 3 H), 1.93 (s, 3 H), 2.08 (s, 3 H), 2.29 (s, 3 H), 3.24 (s, 3 H), 5.53 (s, 1 H); mass spectrum, *m/e* 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95. Found: C, 73.39; H, 8.94. Spectroscopic data of **25**: IR (CCl_4) 1660 (C=O), 1630 (C=C) cm^{-1}; UV λ_{max} 230 nm (ε 9200); ^1H NMR ($CDCl_3$) δ 1.32 (s, 3 H), 1.89 (s, 3 H), 1.98 (s, 6 H), 2.93 (s, 3 H), 6.18 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.7 (q), 14.0 (q), 17.3 (q), 24.9 (q), 51.9 (q), 77.2, 128.5 (d, J_{CH} = 160 Hz), 133.5, 154.0, 159.5, 195.7 (C=O); mass spectrum, found *m/e* 180.115, calcd *m/e* 180.115 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95. Found: C, 72.56; H, 8.98.

$Cu(acac)_2$-Catalyzed Decomposition of 1 in Methanol. To a solution containing 0.60 mmol of **1** in 10 mL of dry methanol was added a solution of 10 mg (0.05 mmol) of copper acetylacetonate in 1 mL of methanol at room temperature. Compound **1** had completely decomposed within 1.5 h according to IR spectroscopy. The solvent was evaporated and the residue subjected to preparative TLC (silica gel, 1:1 hexane/CH_2Cl_2) to afford 50 mg (0.28 mmol, 26% yield) of **24** as the only isolable product; none of **25** had formed as shown by ^1H NMR spectroscopy.

$Rh_2(OAc)_4$-Catalyzed Decomposition of 1 in Methanol. A solution containing 0.57 mmol of **1** in 5 mL of dry methanol was added to a mixture of 0.65 mg (0.003 mmol) of rhodium acetate and 15 mL of dry methanol while the temperature was maintained at −70 °C. The reaction mixture was allowed to warm to 0 °C overnight. Filtration and evaporation of the solvent in vacuo afforded an oil which contained **24** and **25** in yields of 30% and 13%, respectively, as determined by ^1H NMR spectroscopic integration.

Uncatalyzed Decomposition of 1 in Methanol. A solution containing 0.35 mmol of **1** in 5 mL of methanol was allowed to stand for 18 h at room temperature. IR measurements still showed the presence of **1**. When **1** was left in methanol solution for another 24 h, decomposition of **1** was complete according to IR spectroscopy. Removal of the solvent afforded an oil which contained **24** and **25** in yields of 21% and 16%, respectively, as determined by ^1H NMR spectroscopy.

$AgClO_4$-Catalyzed Decomposition of 1 in Vinyl Acetate (Solvent). Synthesis of Dihydrobenzofuran 34. A solution containing 0.70 mmol of **1** in 2 mL of vinyl acetate was added dropwise to a stirred suspension of 21 mg (0.1 mmol) of silver perchlorate and 106 mg (1.0 mmol) of sodium carbonate in 20 mL of vinyl acetate while the reaction temperature was maintained at −70 °C. The mixture was allowed to warm to room temperature overnight. Filtration over Celite and evaporation of the solvent in vacuo furnished an oily residue. Bulb-to-bulb distillation [80–120 °C (0.01 mmHg)] followed by preparative TLC (alumina, 3/1 CH_2Cl_2/hexane) gave 50 mg (0.22 mmol, 31% yield) of **34** as a white solid. Final purification was achieved by repeated crystallization (hexane, methanol) to afford **34** as white crystals: mp 108.4–109.5 °C; IR (KBr) 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (s, 3 H), 2.21 (s, 12 H), 3.0–3.7 (m, 2 H), 6.82 (dd, *J* = 3.0, 6.0 Hz, 1 H); irradiation at δ 6.82 reveals the presence of an AB quartet at δ 3.08 and 3.38 (*J* = 17 Hz); mass spectrum, found *m/e* 234.128, calcd *m/e* 234.126 (M^+). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.76; H, 7.74. Found: C, 71.23; H, 7.66.

$AgClO_4$-Catalyzed Decomposition of 1 in 2,3-Dimethyl-2-butene. Synthesis of Octamethyldihydrobenzofuran (35). The synthesis of **35** was carried out analogously to the preparation of **36** by using 0.60 mmol of **1** and 2 mL of 2,3-dimethyl-2-butene. Purification was obtained by bulb-to-bulb distillation to afford 100 mg (0.43 mmol, 71% yield) of **35** as a slightly yellow oil. An analytically pure sample of **35** was obtained by preparative TLC (alumina, CCl_4) followed by bulb-to-bulb distillation [85–90 °C (0.01 mmHg)]: IR (neat) 1085 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 6 H), 1.27 (s, 6 H), 2.13 (br s, 9 H), 2.24 (s, 3 H); mass spectrum *m/e* 232 (M^+). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.40. Found: C, 82.50; H, 10.40.

$AgClO_4$-Catalyzed Decomposition of 1 in 2-Methylpropene. Synthesis of Phenol 36. A solution containing 1.40 mmol of **1** in 5 mL of hexane was added dropwise to a stirred suspension of 42 mg (0.20 mmol) of silver perchlorate and 212 mg (2.0 mmol) of sodium carbonate in 30 mL of 2-methylpropene while the reaction temperature was maintained at −70 °C. The mixture was allowed to warm to room temperature overnight. The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2 and filtrated over Celite. Evaporation of the solvent in vacuo furnished 370 mg of a brown oil which was purified by bulb-to-bulb distillation [80–100 °C (0.01 mmHg)] to afford 170 mg (0.83 mmol, 59% yield) of **36** as a slightly yellow oil. An analytically pure sample was obtained by applying high-pressure LC (silica gel, 14/86 CH_2Cl_2/hexane): IR (CCl_4) 3520 (OH), 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (br s, 3 H), 2.19 (s, 12 H), 3.40 (br s, 2 H), 4.65 (br s, 1 H), 4.83 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.3 (q), 16.3 (q), 22.5 (q), 35.6 (t, J_{CH} = 125 Hz), 111.1 (t, J_{CH} = 158 Hz), 120.1, 120.8, 127.0, 132.8, 134.0, 144.2, 150.3; mass spectrum, found *m/e* 204.151, calcd *m/e* 204.152 (M^+). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.04; H, 9.73.

$Rh_2(OAc)_4$-Catalyzed Decomposition in 2,3-Dimethyl-2-butene (or Pentane). Synthesis of 47. A solution containing 0.68 mmol of **1** in 2 mL of 2,3-dimethyl-2-butene was added dropwise to a stirred suspension of 0.62 mg (0.004 mmol) of

rhodium acetate and 15 mL of 2,3-dimethyl-2-butene while the temperature was maintained at -70 °C. The mixture was allowed to warm to room temperature with stirring which was continued for 4 days. The residue obtained after removal of the solvent was subjected to preparative TLC (alumina, benzene) to afford 32 mg (0.10 mmol, 30% yield) of **47** as a white solid. Further purification was achieved by repeated crystallization from methanol to provide **47** as white crystals, mp 194.6-196.8 °C. Crystals appropriate to allow an X-ray determination were grown by slow evaporation of a methanol solution of **47**: IR (CCl_4) 1755 (C=O) cm^{-1}; UV (ethanol) λ_{max} 207 nm (43 400), 290 (3060), 336 (92); ^1H NMR ($CDCl_3$) δ 1.17 (s, 6 H), 1.58 (s, 6 H), 2.10 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 2.8 (q), 4.3 (q), 4.5 (q), 12.3 (q), 15.3 (q), 23.2, 40.0, 48.9, 111.8, 114.2, 127.6, 144.0, 207.0 (C=O); mass spectrum, m/e 312 (M^+). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.55; H, 7.70.

Reaction of 1 with *o*-Dihydroxybenzene. Synthesis of 49 and 51. To a solution containing 1.32 mmol of **1** in 10 mL of CH_2Cl_2 was added dropwise a solution of 290 mg (2.64 mmol) of *o*-dihydroxybenzene in 20 mL of CH_2Cl_2 while the temperature was maintained at -80 °C. The mixture was allowed to warm to room temperature overnight. The solvent was removed in vacuo to leave a brown residue. Upon the addition of ether, 157 mg (0.60 mmol, 45% overall yield) of a brown-white precipitate was obtained, consisting of a mixture of **49** and **51** (ratio 5:2, respectively). Crystallization of this precipitate from CH_2Cl_2/hexane and methanol gave 30 mg of **49** as white crystals, mp 127.1-127.4 °C. The combined mother liquors were subjected to high-pressure LC (silica gel, 9/1 CH_2Cl_2/CH_3CN) to furnish 83 mg of **49** (total yield of **49** was 113 mg, 0.40 mmol, 30%) and 43 mg (0.17 mmol, 13%) of **51** as white crystals, mp 121.5-122.1 °C. Crystals of **49** appropriate to allow an X-ray determination were grown from a slowly evaporating methanol solution. Spectroscopic data for **49**: IR ($CHCl_3$) 3540 (OH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.31 (s, 3 H), 1.49 (s, 3 H), 1.58 (s, 3 H), 2.52 (s, 1 H), 5.62 (br s, 1 H), 6.87 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 4.3 (q), 4.7 (q), 7.9 (q), 16.6 (q), 34.6, 43.9, 50.6 (d, J_{CH} = 180 Hz), 71.5, 87.1, 115.5 (d, J_{CH} = 156 Hz), 119.8 (d, J_{CH} = 156 Hz), 121.9 (d, J_{CH} = 162 Hz), 124.7 (d, J_{CH} = 162 Hz), 141.3, 149.0, 187.0 (C=O); mass spectrum, found m/e 258.130, calcd m/e 258.126 (M^+). Spectroscopic data for **51**: IR ($CHCl_3$) 3520 (OH), 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 1.32 (s, 3 H), 1.50 (s, 3 H), 1.56 (s, 3 H), 3.11 (s, 1 H), 5.63 (br s, 1 H), 6.86 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 3.8 (q), 4.0 (q), 5.7 (q), 18.3 (q), 33.8, 47.0, 57.1, 67.1 (d, J_{CH} = 168 Hz), 85.1, 115.5 (d, J_{CH} = 162 Hz), 120.1 (d, J_{CH} = 162 Hz), 120.2 (d, J_{CH} = 162 Hz), 124.2 (d, J_{CH} = 162 Hz), 141.7, 148.5, 184.7 (C=O); mass spectrum, found m/e 258.128, calcd m/e 258.126 (M^+).

Registry No. **1**, 68255-25-4; **2**, 56745-78-9; **3**, 74744-17-5; **4**, 70993-60-1; **5**, 68255-26-5; **6**, 68255-27-6; **7**, 74725-13-6; **8**, 56745-77-8; **9**, 74744-18-6; **11**, 67024-12-8; **14A/14B**, 68255-28-7; **16**, 74725-14-7; **17**, 74744-19-7; **23**, 74725-15-8; **24**, 74725-16-9; **25**, 74725-17-0; **34**, 74725-18-1; **35**, 74725-19-2; **36**, 74725-20-5; **47**, 74725-21-6; **49**, 74725-22-7; **51**, 74725-23-8; acrylonitrile, 107-13-1; dimethyl acetylenedicarboxylate, 762-42-5; tetrachloro-*o*-quinone, 2435-53-2; vinyl acetate, 108-05-4; 2,3-dimethyl-2-butene, 563-79-1; 2-methylpropene, 115-11-7; *o*-dihydroxybenzene, 120-80-9; $AgClO_4$, 7783-93-9; $Cu(Acac)_2$, 13395-16-9; $Rh_2(OAc)_4$, 11071-42-4.

Synthesis of 1,2,3-Decanetriol Stereoisomers

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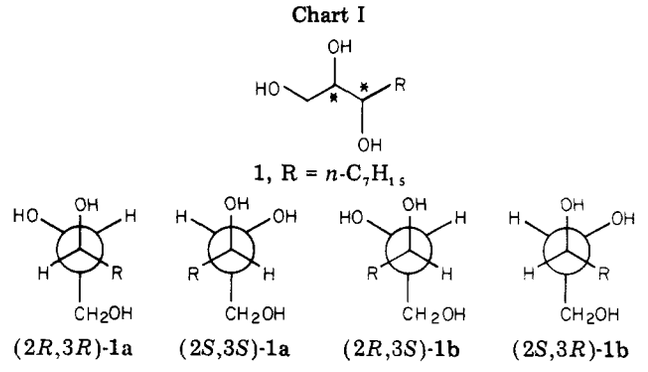
The synthesis and ^{13}C NMR spectra of 1,2,3-decanetriol stereoisomers are described. High enantiomeric purity triols are obtained by chromatographic resolution of diastereomeric carbamates derived from 1-decyn-3-ol and (*R*)-1-(1-napthyl)ethylamine. The triol is obtained by conversion of the acetylene to an olefin, stereoselective epoxidation with *tert*-butyl hydroperoxide and a transition-metal catalyst, and stereospecific ring opening of the epoxide with KOH.

In connection with ^{13}C NMR relaxation studies of highly associated molecules, interesting results have been obtained from the study of 1,2-decanediol.[2] To continue these studies and to further clarify the mechanism of this novel relaxation behavior, we found it desirable to prepare and study the relaxation properties of 1,2,3-alkanetriols. To eliminate spectral complication and to examine possible differences in NMR chemical shift and relaxation properties of the diastereomers and enantiomers in racemic and enantiomerically pure form, we prepared the four stereoisomers of 1,2,3-decanetriol (Chart I, **1**).

Problems attending the synthesis of optically active materials include the determinations of absolute configuration and enantiomeric composition of the final product. We report a relatively simple synthesis of 1,2,3-alkanetriols applied to **1** which allows direct assignment of the absolute configuration and enantiomeric purity as a consequence of the reaction sequence, NMR spectral properties, and chemical properties of key intermediates in the synthesis.

Chart I



Results and Discussion

The synthesis of 1,2,3-decanetriol (**1**) is described in Scheme I. The preparation of optically active **1** hinges upon the chromatographic separation of the enantiomers of propargyl alcohol (**2**) via their diastereomeric carbamate

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