Synthesis of 1,5-Disubstituted Tricyclo[2.1.0.0²,⁵]pentanes. The Crystal and Molecular Structures of 1,5-Bis(acetoxymethyl)tricyclo[2.1.0.0²,⁵]pentan-3-one[†]

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A series of substituted cyclopropene esters has been synthesized by the dirhodium(II) tetraacetate catalyzed addition of ethyl and *tert*-butyl diazoacetate to 1,4-diacetoxy-2-butyne. Selective hydrolysis converted ethyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate (II) to ethyl 1,2-bis(hydroxymethyl)cyclopropene-3-carboxylate (III) and then to 1,2-bis(hydroxymethyl)cyclopropene-3-carboxylic acid (IV). Acetic anhydride treatment of IV yielded 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylic acid (V). However, the latter was more readily prepared by trifluoroacetic acid promoted deesterification of *tert*-butyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate (VI). The rhodium carboxylate catalyzed reaction leading to VI also yielded a small amount of *exo,exo*-di-*tert*-butyl 1,3-bis(acetoxymethyl)bicyclo[1.1.0]butane-2,4-dicarboxylate (VII) as a side product. The carboxylic acid V was converted to the acid bromide, 1,2-bis(acetoxymethyl)cyclopropene-3-carbonyl bromide (VIII), which upon treatment with diazomethane at −78 °C yielded 1,2-bis(acetoxymethyl)-3-(diazoacetyl)cyclopropene (IX). The latter reaction yields 1,2-bis(acetoxymethyl)-3-(bromoacetyl)cyclopropene (X) when worked up with acetic acid before completion of the reaction. A side product pyrazoline diazo ketone, XI, was formed by the addition of diazomethane across the double bond of IX. Treatment of IX with Rh₂(OAc)₄ yielded 1,5-bis(acetoxymethyl)tricyclo[2.1.0.0²,⁵]pentan-3-one (XII). The keto diacetate XII is readily hydrolyzed to 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0²,⁵]pentan-3-one (XIII) or converted to the ketals: 1,5-bis(acetoxymethyl)-3,3-diethoxytricyclo[2.1.0.0²,⁵]pentane (XVa) and 1′,5′-bis(acetoxymethyl)spiro[1,3-dioxolane-2,3′-tricyclo[2.1.0.0²,⁵]pentane] (XVb). The latter are readily hydrolyzed to the corresponding diols: 1,5-bis(hydroxymethyl)-3,3-diethoxytricyclo[2.1.0.0²,⁵]pentane (XVa) and 1′,5′-bis(hydroxymethyl)spiro[1,3-dioxolane-2,3′-tricyclo[2.1.0.0²,⁵]pentane] (XVIb). An X-ray crystal structure of the tricyclic keto diacetate XII reveals an extremely short (1.416 Å) bridging carbon–carbon single bond.

Doering and Pomerantz[1] and Masamune[2] synthesized the first members of the tricyclo[2.1.0.0²,⁵]pentan-3-one series, the former[1] by copper-catalyzed internal cyclization of 1,2-dimethyl-3-(diazoacetyl)cyclopropene[3] and the latter[2] by photolysis of 1,2-diphenyl-3-(diazoacetyl)cyclopropene. The structures are firmly established by spectroscopic data[1,2] and by X-ray crystal structure analysis.[4a,b] The results of the X-ray structural investigation are of immediate interest from a theoretical standpoint because of what is revealed of the tightly coupled and unusual bonding in the bridged bicyclo[1.1.0]butane series.[4c] Irngartinger and Lukas found a linear correlation between the flap angle θ and the C_1–C_3 bond length (see below) in a

series of rigidly held bridged bicyclobutanes. Their work also revealed an extremely short C_1–C_3 *single* bond (1.408 Å) in the 1,5-dimethyltricyclo[2.1.0.0²,⁵]pentan-3-one system. Very recently Dunitz and Sziemies and their collaborators carried out a very careful study of a bicyclobutane further bridged at the 1- and 3-positions by a three-carbon chain (a [3.1.1]propellane).[4d] The angular distortion at C_1 and C_3 dramatically increases the C_1–C_3 bond length to 1.57 Å and decreases the internuclear electron density to nonbonding levels.[4d]

Clearly, the ability to synthesize other members of this family will be important as exploration of the unusual bonding situation in this series continues. This paper presents a synthetic route to the substituted tricyclo-[2.1.0.0²,⁵]pentan-3-ones together with an X-ray crystal structure which buttresses the earlier conclusions of Irngartinger and Lukas.[4a]

In the present series of experiments, catalysis of diazo ester addition to olefins and acetylenes by dirhodium(II) tetraacetate[5a] has been extended to include the first use of the rhodium catalyst in an intramolecular diazo ketone cycloaddition reaction.[5b] This procedure now makes possible 30–40% yields of the rare tricyclo[2.1.0.0²,⁵]pentanone skeleton.

Synthesis

Addition of ethyl diazoacetate to excess 1,4-diacetoxy-2-butyne (I) containing a catalytic amount of dirhodium(II) tetraacetate resulted in controlled nitrogen evolution. The reaction required no heating and proceeded smoothly at

(1) W. v. E. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964).
(2) S. Masamune, *J. Am. Chem. Soc*, 86, 735 (1964).
(3) See also G. Maier, H. P. Resinauer, and H. A. Freitag, *Tetrahedron Lett.*, 121 (1978).
(4) (a) H. Irngartinger and K. L. Lukas, *Angew. Chem., Int. Ed. Engl.*, 18, 694 (1979). (b) See also J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J. Am. Chem. Soc.*, 89, 2792 (1967), and C. S. Gibbons and J. Trotter, *J. Chem. Soc. A*, 2027 (1967), in which the X-ray crystal structure of 1,5-diphenyltricyclo[2.1.0.0²,⁵]pent-3-yl *p*-bromobenzoate at 0.05-Å resolution is reported. (c) M. N. Paddon-Row, K. N. Houk, P. Dowd, P. Garner, and R. Schappert, *Tetrahedron Lett.*, 4799 (1981). (d) P. Chakrabati, P. Seiler, J. D. Dunitz, A.-D. Schütter and G. Sziemies, *J. Am. Chem. Soc.*, 103, 7378 (1981).
(5) (a) N. Petiniot, A. J. Auciaus, A. F. Noels, A. J. Hubert, and P. Teyssie, *Tetrahedron Lett.*, 1239 (1978); A. J. Hubert, A. F. Noels, A. J. Auciaux, P. Teyssie, *Synthesis*, 600 (1976); A. J. Auciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and P. Teyssie, *J. Org. Chem.*, 45, 695 (1980). (b) For a recent comprehensive review of intramolecular diazo ketone cycloaddition reactions see S. D. Burke and P. A. Grieco, *Org. React.*, 26, 361 (1978). (c) P. Dowd, *J. Am. Chem. Soc.*, 88, 2587 (1966).

AcOCH$_2$C≡CCH$_2$OAc $\xrightarrow[\text{Rh}_2(\text{OAc})_4]{\text{N}_2\text{CHCOOEt}}$
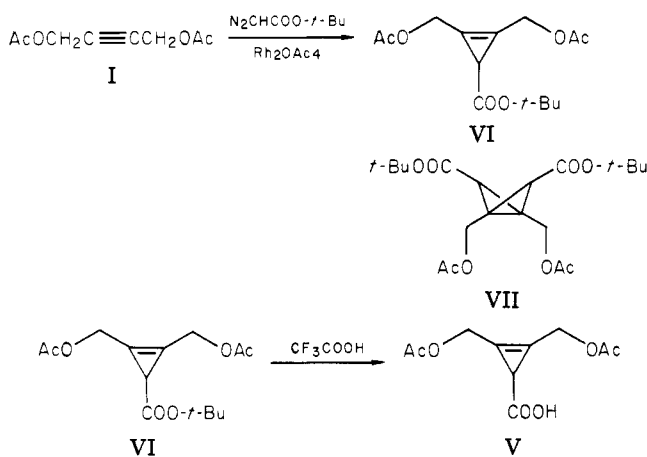
I

II
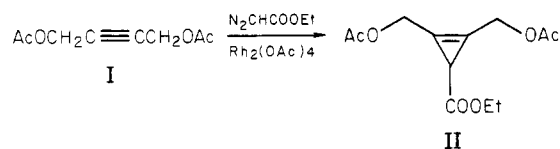
room temperature. The desired ethyl 1,2-bis(acetoxymethyl)cyclopropenecarboxylate (II) was isolated in 30% yield as a distillable liquid.

The ester II is converted to the bis(hydroxymethyl) ester III by treatment with potassium carbonate in ethanol and

II $\xrightarrow[\text{K}_2\text{CO}_3]{\text{EtOH}}$ III

$\downarrow$ NaOH, MeOH

IV $\xrightarrow{\text{Ac}_2\text{O}}$ V
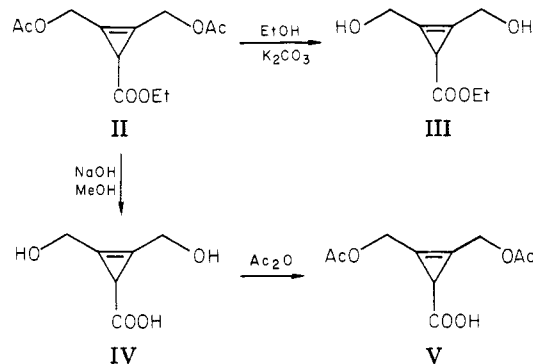
to the bis(hydroxymethyl) carboxylic acid IV by using sodium hydroxide in methanol. The acid IV was transformed by treatment with acetic anhydride into the bis(acetoxymethyl) carboxylic acid V. The latter is required for subsequent development; accordingly, a more concise route to V was devised.

The butyne diacetate I was reacted with *tert*-butyl diazoacetate[6] in the presence of the rhodium catalyst, yielding (65%) the bis(acetoxymethyl) *tert*-butylester VI,

AcOCH$_2$C≡CCH$_2$OAc $\xrightarrow[\text{Rh}_2\text{OAc}_4]{\text{N}_2\text{CHCOO-}t\text{-Bu}}$

I

VI

VII

VI $\xrightarrow{\text{CF}_3\text{COOH}}$ V

which was purified by chromatography. In addition, the double adduct *exo,exo*-di-*tert*-butyl 1,3-bis(acetoxymethyl)bicyclo[1.1.0]butane-2,4-dicarboxylate (VII) was isolated in approximately 2% yield in the course of the chromatographic purification of VI. The bis(acetoxymethyl) carboxylic acid V was then produced in 80% yield on treatment on the *tert*-butyl ester VI with trifluoroacetic acid at room temperature. The carboxylic acid V was reacted with excess oxalyl bromide to yield the acid bromide VIII. The latter was then treated at −78 °C with ethereal diazomethane and maintained at that temperature for 40–60 h. When diazo ketone formation was complete, the reaction was worked up and the diazoketone IX isolated as a stable yellow crystalline solid, mp 68–69 °C.

V $\xrightarrow{(\text{COBr})_2}$ VIII $\xrightarrow[-78 °C]{\text{CH}_2\text{N}_2}$ →

IX

X
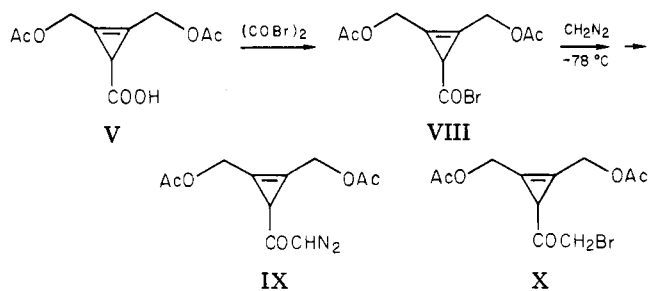
Earlier attempts to prepare the diazo ketone IX according to conventional procedures by way of the acid chloride at 0 °C did yield a diazo ketone. However, it was apparent from the NMR spectrum that the product was not the desired diazo ketone X; instead, the somewhat unstable pyrazoline diazo ketone XI was formed.

XI
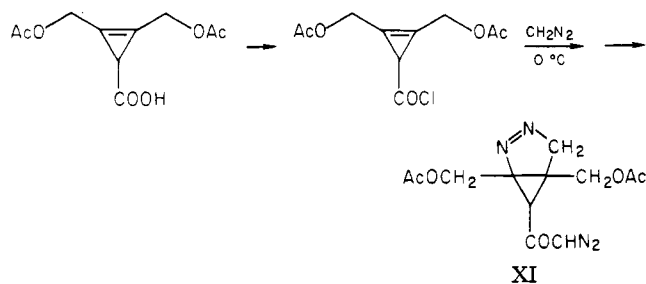
In one sense this is not surprising. The cyclopropene double bond is highly reactive, and adduct formation between diazomethane and olefins is not unknown.[5c] What was surprising was that adduct formation did not occur in the Doering and Pomerantz sequence.[1] No difficultly was experienced in forming their diazo ketone under normal circumstances through the acid chloride at 0 °C. Apparently, the inductive effect of the acetoxy groups is just sufficient to lower the barrier to cycloaddition. It is ironic that the same electron-withdrawing substituents which dampen the reactivity of the triple bond, necessitating the use of the rhodium catalyst, also serve to increase the reactivity of the cyclopropene double bond toward 1,3-dipolar cycloaddition of diazomethane. In neither case was it anticipated that such a large perturbation in reactivity would result from the substituents. Pyrazoline formation also occurred when the butyne was substituted with benzoyloxy, chloro, and methoxy groups.

The key transformation of the sequence, the internal cycloaddition of the diazo ketone to the cyclopropene double bond, was carried out by slow addition of a chloroform solution of IX to a catalytic amount of di-

IX $\xrightarrow{\text{Rh}_2\text{OAc}_4}$ XII
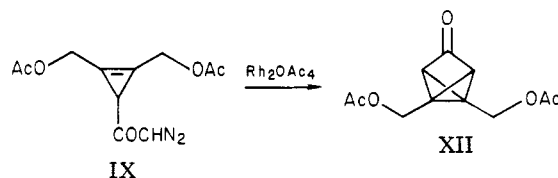
rhodium(II) tetraacetate in chloroform at 60 °C. Chromatography, following workup of the reaction mixture, yielded the tricyclic ketone XII in 30–40% yield as a crystalline solid, mp 57–58 °C. Spectral data supporting the tricyclopentanone structure XII are reported in the Experimental Section and are in excellent accord with the assigned structure. In addition, the structure of the tricyclic ketone XII was established beyond doubt by the X-ray crystallographic structure determination described in the section which follows.

The dirhodium tetraacetate catalyst has been used in a variety of applications involving the addition of diazo

(6) M. Regitz, J. Hocker, and A. Liedhegener, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 179.

esters to double and triple bonds. The experiment described above extends the method to encompass the intramolecular addition of a diazo ketone to a double bond. Prior to the advent of the dirhodium tetraacetate catalyst,[5a] only the dimethyl and di-*n*-propyl derivatives of the aliphatic tricyclo[2.1.0.0]pentanones were known. They were obtained in low yield from the copper-catalyzed reactions. The 30–40% yields observed in the rhodium acetate catalyzed reaction, while not ideal, make this series much more accessible than it was formerly. In addition, the acetoxy groups may be converted to a wide variety of other functional groups, and the bridging bond may be cleaved to provide access to a number of functionalized bicyclo[1.1.1]pentanes.

The diacetate XII is the central synthetic intermediate for further elaboration of this series. In order to take advantage of it, one needs to be able to remove the acetate groups and to protect the ketone. Both operations are readily accomplished as described below.

The acetate groups are easily removed by ethanolysis, with potassium carbonate in ethanol, yielding the keto diol XIII. In one experiment, the monoactate XIV was also
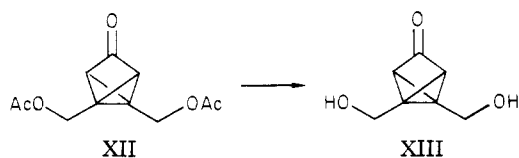

isolated in the course of the chromatographic purification of the diol XIII. The keto group of the diacetate XII may be protected as the diethyl and ethylene ketals XVa and XVb. The latter are readily converted to the ketal diols XVIa and XVIb respectively.

XVa, R = Et
b, R, R = -CH₂CH₂-

XVIa, R = Et
b, R, R = -CH₂CH₂-
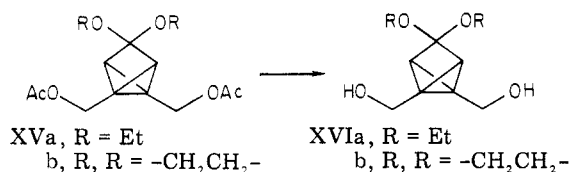
### X-ray Crystal Structure Analysis

The structure of 1,5-bis(acetoxymethyl)tricyclo-[2.1.0.0^{2,5}]pentan-3-one (XII) has been established by X-ray diffraction.[7] The molecular structure with the bond lengths and bond angles is shown in Figure 1. The molecular dimensions of XII compare well with the corresponding values of the parent compound 1,5-dimethyl-tricyclo[2.1.0.0^{2,5}]pentan-3-one.[4a] Chemically equivalent values, determined independently in the crystal, also compare very well within the limits of experimental accuracy.

The bond between the bridgehead carbon atoms, C(2) and C(3) in the bicyclo[1.1.0]butane part of XII, is very

XII
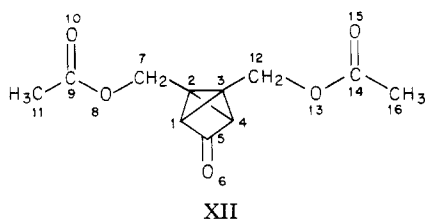
short (1.416 (2) Å). This bond has pronounced p charac-

(7) Preliminary communication: H. Irngartinger, A. Goldmann, R. Schappert, P. Garner, and P. Dowd, *J. Chem. Soc., Chem. Commun.*, 455 (1981).
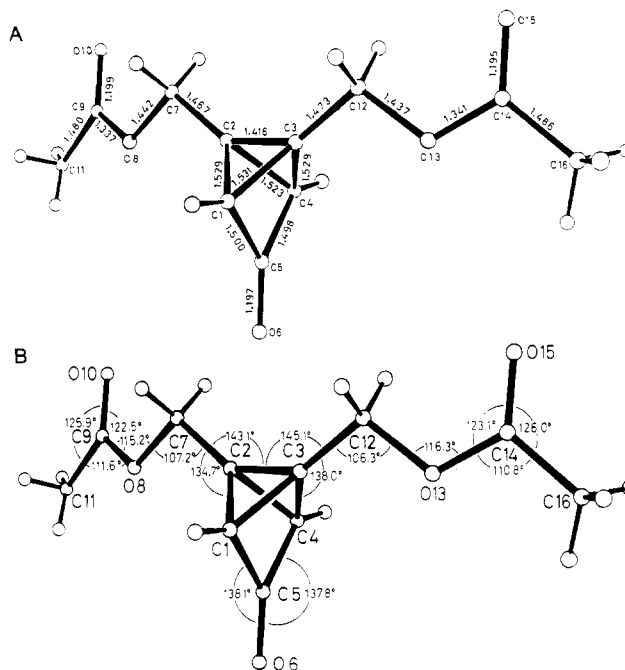
Figure 1. Structure of compound XII with (A) bond distances and (B) angles as indicated. The estimated standard deviations are 0.002–0.006 Å and 0.1–0.3°, respectively.

ter.[8] It has been shown[4a] that the length of this bond in bicyclo[1.1.0]butane derivatives is dependent on the dihedral angle θ between the planes of the two cyclopropane rings.[4c] In XII this angle has a value of 95.7°. As a consequence of the bridging carbonyl group, the nonbonding contact C(1)···C(4) (2.006 (3) Å) is very short. The orientations and conformations of the two acetoxymethyl substituents, relative to the tricyclic system, are very similar. The nonhydrogen atoms of each group lie in a plane with an average deviation of 0.009 Å. The dihedral angles of these groups with respect to the plane through the atoms C(2), C(3), C(5), and O(6), which bisects the bicyclo-[1.1.0]butane system, are 11.7° and 19.0°. This orientation is determined by the energetically favorable antiperiplanar conformation along the C(2)–C(7) and C(3)–C(12) bonds. The torsion angles C(2)–C(3)–C(12)–O(13) and C3)–C-(2)–C(7)–O(8) are 172.3° (3) and −170.8° (2), respectively.

Experimental Section

Unless otherwise stated, proton NMR spectra were taken at 60 MHz on a Varian T-60 instrument. Thin-layer chromatograms were carried out on silica gel plates. Substances were detected by development as spots with iodine, by spraying with dilute sulfuric acid containing salicylaldehyde followed by charring, or by using ultraviolet light.

Ethyl 1,2-Bis(acetoxymethyl)cyclopropene-3-carboxylate (II). Ethyl diazoacetate (96.7 g, 0.848 mol) was dissolved in 1,4-diacetoxy-2-butyne (112.6 g, 0.662 mol), placed in a side-arm dropping funnel, and added dropwise under an atmosphere of nitrogen over a period of 17 h to a stirred mixture of dirhodium(II) tetraacetate (0.932 g, 0.002 mol) and 1,4-diacetoxy-2-butyne (350.7 g, 2.061 mol). The temperature of the reaction mixture varied between 26 and 36 °C.

The reaction mixture was filtered through a Celite pad, which was washed with 100 mL of ether. The filtrate was cooled in an

(8) M. Pommerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966); W. R. Moore and R. C. Costin, *ibid.*, **93**, 4910 (1971); M. D. Newton and J. M. Schulman, *ibid.*, **94**, 767 (1972); P. Bischof, R. Gleiter, and E. Müller, *Tetrahedron*, **32**, 2769 (1976); M. Horner and S. Huenig, *J. Am. Chem. Soc.*, **99**, 6122 (1977); G. Szeimies, J. Harnisch, and K. H. Stadler, *Tetrahedron Lett.*, 243 (1978); H. Finkelmeier and W. Lüttke, *J. Am. Chem. Soc.*, **100**, 6261 (1978).

ice bath, and excess 1,4-diacetoxy-2-butyne crystallized upon seeding. The crystallization process was repeated twice at −15 °C overnight to yield 138.5 g of pale yellow solid butyne I and 550.9 g of red liquid.

The latter was chromatographed on 1000 g of silica gel. Elution was begun with 90:10 hexane–ethyl acetate and continued until the butyne (R_f 0.4) began to appear, and then the solvent polarity was increased to 80:20 hexane–ethyl acetate. The latter was used until the desired cyclopropene II (R_f 0.3, 70:30 hexane–ethyl acetate) began to appear, and then the solvent polarity was increased to 70:30 hexane–ethyl acetate and continued to the end of the chromatography. The total amount of ethyl 2,3-bis-(acetoxymethyl)cyclopropene-3-carboxylate (II) obtained was 69.5 g (29%), bp 98–102 °C (6 × 10^{-4} mm).

The proton NMR spectrum (CCl$_4$) of II showed a four-proton acetoxymethyl singlet at δ 4.89, a two-proton ethyl ester quartet (J = 7 Hz) at δ 4.01, a one-proton cyclopropene methine singlet at δ 2.16, a six-proton acetate methyl singlet at δ 2.04, and a three-proton ethyl ester triplet (J = 7 Hz) at δ 1.13. The partially coupled ^{13}C NMR spectrum (15.03 MHz, CDCl$_3$) showed an ethyl ester carbonyl singlet at 174.05 ppm, an acetate carbonyl singlet at 170.28 ppm, a vinyl singlet at 106.09 ppm, a triplet at 60.48 ppm due to the methylene group of the ethyl ester, an acetoxymethyl triplet at 56.9 ppm, a quartet at 14.31 ppm due to the methyl group of the ethyl ester, a quartet at 23.57 ppm due to the acetate methyl group, and a cyclopropene methine doublet at 22.49 ppm. The infrared spectrum (neat) showed carbonyl bands at 1749 and 1723 cm^{-1} together with a cyclopropene double bond stretching vibration at 1910 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (relative intensity) 256 (M$^+$), 183 (30, M$^+$ − COOEt), 154 (19), 126 (18), 43 (100, CH$_3$OC$^+$); exact mass calcd for C$_9$H$_{11}$O$_4$ 183.0657, found 183.0658.

Ethyl 1,2-Bis(hydroxymethyl)cyclopropene-3-carboxylate (III). Ethyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate (II; 14.665 g, 0.057 mol) was dissolved in 100 mL of ethanol and cooled to 5 °C in an ice bath. Anhydrous potassium carbonate (16.395 g, 0.119 mol) was added slowly with stirring. The reaction mixture was allowed to warm to room temperature and stirred for 14 h. The amber suspension was concentrated on a rotary evaporator, diluted with 100 mL of water, and extracted with four 200-mL portions of ethyl acetate. The organic extracts were combined, dried with sodium sulfate, filtered, and evaporated to yield 8.7 g of amber oil. The oil was chromatographed rapidly on 50 g of silica gel. Elution with 50:50 hexane–ethyl acetate yielded 7.4 g (76%) of III as a clear yellow oil after removal of the solvent.

The proton NMR spectrum (CDCl$_3$) of III showed a four-proton hydroxymethyl singlet at δ 4.52, a two-proton broad hydroxyl singlet at δ 4.37, a two-proton ester methylene quartet (J = 7 Hz) at δ 4.06, a one-proton cyclopropene methine singlet at δ 2.34, and a three-proton methyl triplet (J = 7 Hz) at δ 1.23. The infrared spectrum (neat) showed very broad hydroxyl absorption at 3700–2500, together with ester carbonyl absorption at 1700 cm^{-1} and cyclopropene double bond absorption at 1898 cm^{-1}. The mass spectrum (70 eV) showed m/e (relative intensity) 173 (3.6, M + H), 144 (4.3), 127 (15, M$^+$ − OEt), 99 (100, M − CO$_2$Et), and 81 (8.6); exact mass calcd for C$_5$H$_7$O$_2$ 99.0446, found 99.0446.

1,2-Bis(hydroxymethyl)cyclopropene-3-carboxylic Acid (IV). Ethyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate (II; 4.176 g, 0.016 mol) was dissolved in 50 mL of methanol, and sodium hydroxide (3.131 g, 0.078 mol) was added. The orange reaction mixture was stirred at room temperature overnight and then concentrated to an oily solid. The solid was dissolved in 25 mL of water and extracted with two 100-mL portions of ether. The aqueous layer was acidified in an ice bath with 10 mL of concentrated hydrochloric acid and extracted with five 200-mL portions of ethyl acetate. The combined ethyl acetate layers were dried with sodium sulfate and filtered, and the solvent was concentrated, yielding 0.897 g (38%) of off-white crystals, mp 108–109 °C. The acidic aqueous layer was extracted continuously with ethyl acetate for 1 day to give 0.466 g (20%) of off-white crystals, mp 106–108 °C. Recrystallization of the total solid from hot ethyl acetate gave 0.992 g (42%) of white crystals of the diol acid IV, mp 109–110 °C.

The proton NMR spectrum (acetone-d_6) showed a four-proton hydroxymethyl singlet at δ 4.47, a one-proton cyclopropane

methine singlet at δ 2.21, and a broad hydroxyl singlet at δ 5. The infrared spectrum (KBr) showed a very broad hydrogen bonded hydroxyl and carboxylic acid resonance at 3500–2100 cm^{-1}, a cyclopropene double bond absorption at 1908 cm^{-1}, and a carbonyl band at 1684 cm^{-1}. The mass spectrum (70 eV) showed peaks at m/e (relative intensity) 144 (5, M$^+$), 127 (23), 126 (32), 99 (100, M$^+$COOH), 98 (35), 97 (64), 96 (24), 86 (19), 82 (46), 81 (16), 79 (39), 78 (23), and 77 (23); exact mass calcd for C$_6$H$_8$O$_4$ 144.0423, found 144.0420.

***tert*-Butyl 1,2-Bis(acetoxymethyl)cyclopropene-3-carboxylate (VI).** A solution of 0.387 g (0.85 mmol) of dirhodium(II) tetraacetate, dried at 100 °C (0.001 mm) for 12 h, and 96.71 g (0.57 mol) of freshly distilled 1,4-diacetoxy-2-butyne (I) was placed under a nitrogen atmosphere at 27 °C, and 20.12 g (0.14 mol) of freshly distilled *tert*-butyl diazoacetate[6] was added dropwise over a 22-h period. When the addition was complete, the reaction mixture was stirred an additional 1 h, then diluted with 150 mL of 50:50 hexane–ether, and stored at −15 °C to induce crystallization of the excess butyne I. After 10 h the precipitate was collected, and the mother liquor was stripped of solvent, yielding 34.30 g of crude cyclopropene VI which was chromatographed on 1000 g of silica gel. Elution with 1500 mL of 5:1 hexane–ethyl acetate, 2200 mL of 3.5:1 hexane–ethyl acetate, and 2000 mL of 2:1 hexane–ethyl acetate yielded 21.95 g (53%) of cyclopropene VI as a clear oil in the latter fractions.

The proton spectrum NMR (CDCl$_3$) of VI showed a nine-proton *tert*-butyl methyl singlet at δ 1.43, a six-proton acetate methyl singlet at δ 2.08, a one-proton cyclopropenyl methine singlet at δ 2.30, and a four-proton acetoxy methylene singlet at δ 4.97. The fully coupled ^{13}C spectrum (15.03 MHz, CDCl$_3$) showed an ester carbonyl doublet (^2J = 9.77 Hz) at 172.95 ppm, a broad acetate carbonyl singlet at 169.50 ppm, a broad vinyl singlet at 106.22 ppm, a broad quaternary carbon singlet at 79.45 ppm, a methylene triplet (^1J = 152.34 Hz) at 56.97 ppm, a *tert*-butyl methyl quartet (^1J = 126.30 Hz) at 27.83 ppm, and acetate methyl quartet (^1J = 129.56 Hz) at 20.88 ppm, and a cyclopropene methine doublet (^1J = 177.73 Hz) at 24.30 ppm. The infrared spectrum (CCl$_4$) showed cyclopropene double bond adsorption at 1905 cm^{-1}, acetate carbonyl absorption at 1747 cm^{-1}, and *tert*-butyl ester carbonyl absorption at 1720 cm^{-1}. The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 183 (100, M$^+$ − COO-t-Bu), 166 (3, M$^+$ − 20Ac), 124 (6, M$^+$ − COO-t-Bu − OAc); exact mass calcd for C$_9$H$_{11}$O$_4$ 183.0657, found 183.0656. Anal. Calcd for C$_{14}$H$_{20}$O$_6$: C, 59.14; H, 7.09. Found: C, 59.71; H, 6.78.

Di-*tert*-butyl 1,3-Bis(acetoxymethyl)bicyclo[1.1.0]butane-2,4-dicarboxylate (VII). An early fraction from the column chromatography of the *tert*-butyl ester VI yielded 7.1 g of yellow oil. After the sample was allowed to stand at room temperature for a few days, large white crystals formed in the oil. They were collected and washed with hexane. Two crops were obtained in this manner, weighing 771 and 808 mg, respectively. The crystals from both crops had melting point of 101–102 °C. Recrystallization from *n*-pentane gave product with a melting point of 102–102.5 °C. This substance was identified as di-*tert*-butyl 1,3-bis(acetoxymethyl)bicyclo[1.1.0]butane-2,4-dicarboxylate (VII).

The NMR spectrum (300 MHz, CDCl$_3$) showed a four-proton acetoxymethyl singlet at δ 2.059, a two-proton methine singlet at δ 1.519, and an 18-proton singlet at δ 1.507. The infrared spectrum in carbon tetrachloride showed ester carbonyl absorption at 1724 cm^{-1}. The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 325 (2; M − O-t-Bu), 286 (9), 269 (2), 227 (37), 226 (26), 208 (14), 184 (9), 167 (18), 166 (23), 140 (11), 139 (9), 123 (7), 122 (11), 121 (12), and 57; exact mass calcd for C$_{16}$H$_{21}$O$_7$ 325.1287, found 325.1279. Anal. Calcd for C$_{20}$H$_{30}$O$_8$: C, 60.28; H, 7.60. Found: C, 60.53; H, 7.70.

1,2-Bis(acetoxymethyl)cyclopropene-3-carboxylic Acid (V). *tert*-Butyl 1,2-bis(acetoxymethyl)cyclopropene-3-carboxylate VI (11.654 g, 0.046 mol) was cooled to 0 °C, and trifluoroacetic acid (23.763 g, 0.208 mol) was added over a period of 15 min. At the outset the temperature of the exothermic reaction was kept below 10 °C, and then the reaction was stirred and allowed to warm to 20 °C over a 3-h period. Excess trifluoroacetic acid was removed at room temperature under vacuum, yielding 15.034 g of yellow oil. The oil was dissolved in 25 mL of ether, treated with Nuchar C-190, and filtered through Super-Cel. Crystallization yielded 6.385 g (68%) of white prisms, mp 70–71 °C.

The proton NMR spectrum (CDCl₃) showed a one-proton broad carboxylic acid singlet at δ 10.5–10.8, a four-proton acetoxymethyl singlet at δ 5.01, a one-proton cyclopropene methine singlet at δ 2.39, and a six-proton acetate methyl singlet at δ 2.11. The fully coupled carbon-13 NMR spectrum showed a carboxylic acid carbonyl doublet (^2J = 10 Hz) at δ 179.97, an acetate carbonyl quartet (^2J = 8.3 Hz) at δ 170.23, a vinyl triplet (^2J = 6 Hz) at δ 105.65, a methylene triplet (^1J = 152.45) at δ 56.92, an acetate methyl quartet (^1J = 129.5) at δ 23.50, and a cyclopropene methine doublet (^1J = 174 Hz) at δ 20.27. The infrared spectrum (CHCl₃) showed broad carboxyl absorption at 3600–2300 cm⁻¹, cyclopropene double bond absorption at 1914 cm⁻¹, and carbonyl absorption at 1742 and 1698 cm⁻¹. The mass spectrum (15 eV) showed signals at m/e (relative intensity) 183 (47, M⁺ − COOh − H) and 126 (100, M⁺ − Ac₂O); exact mass calcd for C₉H₁₁O₄ 183.0657, found 183.0659. The ultraviolet spectrum (EtOH solvent) showed λ_max 224 nm (ε 648). Anal. Calcd for C₁₀H₁₂O₆: C, 52.63; H, 5.30. Found: C, 52.95; H, 5.27.

1,2-Bis(acetoxymethyl)-3-(diazoacetyl)cyclopropene (IX). 1,2-Bis(acetoxymethyl)cyclopropenecarboxylic acid V (10.009 g, 0.044 mol) was placed in a dry 100-mL flask. The apparatus was placed under positive nitrogen pressure, oxalyl bromide (12.049 g, 0.056 mole) was added at 0 °C, and the reaction mixture was stirred and allowed to warm to 20 °C over a period of 4 h. The excess reagent was then removed, yielding 14.953 g of pale orange, oily acid bromide VIII.

The proton NMR spectrum of the crude acid bromide VIII (CCl₄) showed a four-proton acetoxymethyl singlet at δ 4.94, a one-proton cyclopropene methine singlet at δ 2.68, and a six-proton acetate methyl singlet at δ 2.08. The infrared spectrum (CCl₄) showed cyclopropene double bond absorption at 1915 cm⁻¹, carbonyl bromide absorption at 1791 cm⁻¹, and acetate carbonyl absorption at 1756 cm⁻¹.

The acid bromide VIII was dissolved in 5 mL of ether (freshly distilled from sodium–benzophenone ketyl solution) and added with stirring to 540 mL of 0.4 M ethereal diazomethane solution at −71 to −78 °C over a 1-h period.

After the mixture had been allowed to stand at −78 °C for 38 h, a 1-mL aliquot was removed from the reaction and quenched at −78 °C with 5 drops of acetic acid. After the mixture warmed to room temperature, 25 mL of diethyl ether was added, and the solution was washed with 5 mL of saturated sodium bicarbonate solution. The aqueous layer was saturated with sodium chloride and separated. The ether layer was dried over sodium sulfate and filtered, and the solvent was removed, yielding 33 mg of yellow oil whose NMR spectrum showed a singlet at δ 3.8 indicating the presence of the bromomethyl ketone X. The reaction was judged to be 85% complete and was allowed to stand at −78 °C for an additional 24 h. At this point a second 1-mL aliquot was worked up, and the reaction was judged to be complete following examination of the NMR spectrum as described above.

Acetic acid (20 mL) was added at −75 °C, and the reaction mixture was stirred for 5 min. The dry ice/acetone bath was removed, and the reaction mixture was stirred and allowed to warm to approximately 0 °C under aspirator vacuum over a 1-h period. The resulting suspension was poured into a 1-L separatory funnel and washed with four 50-mL portions of saturated sodium bicarbonate solution. The combined aqueous layers were made basic by the addition of 14 g of solid sodium bicarbonate, were saturated with sodium chloride, and were extracted with 500 mL of ether. After the mixture was dried, the ether was removed at 30 °C to give 14.122 g of a brown oily solid. Chromatography was carried out on a column equipped with an ice-cold water cooled jacket by using 200 g of silica gel and eluting with 50:50 hexane–ethyl acetate. The eluate was collected in 75-mL fractions. The first yellow band collected in fractions 15–21 was the desired diazo ketone IX, R_f 0.45 (2:1 hexane–ethyl acetate). These fractions were combined, and the solvent was removed to give 7.341 g of yellow solid, mp 65–68 °C. The yellow solid was recrystallized from ether at room temperature, yielding 6.953 g (63%) of yellow solid, mp 67–69 °C.

The proton NMR spectrum (60 MHz, CDCl₃) showed a six-proton acetate methyl singlet at δ 2.04, a one-proton cyclopropene methine singlet at δ 2.44, a four-proton acetoxymethyl singlet at δ 4.97, and a one-proton diazomethyl carbonyl singlet at δ 5.22. The infrared spectrum (CCl₄) showed a diazo band at 2100 cm⁻¹,

a cyclopropene double bond stretching band at 1910 cm⁻¹, and acetate and diazocarbonyl absorption at 1750 and 1630 cm⁻¹. The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 183 (100, M⁺ − COCHN₂), 150 (2.7), 123, 122 (5.4, 5.7, M⁺ − COCHN₂ − HOAc), 99 (4.5, 94 (4.2), 81 (8.9), 43 (44.7); exact mass calcd for C₉H₁₁O₄ 183.0657, found 183.0659.

Further elution of the column above yielded, in fractions 24–28, a second diazo ketone which proved to be the cyclopropyl-pyrazoline XI, a yellow liquid.

The NMR spectrum of XI (300 MHz, CDCl₃) showed a one-proton cyclopropyl singlet at δ 1.134, a six-proton acetate methyl singlet at δ 2.055, a two-proton acetoxymethyl AB quartet (J = 12.33 Hz) at δ 4.575 and 4.637, a two-proton pyrazoline AB quartet (J = 19.806 Hz) at δ 4.714 and 4.863, and a two-proton acetoxymethyl AB quartet (J = 12.934 Hz) at δ 4.983 and 5.269. The infrared spectrum (CCl₄) showed a strong diazo band at 2110 cm⁻¹, strong acetate carbonyl absorption at 1742 cm⁻¹, and diazo carbonyl absorption at 1640 cm⁻¹. The mass spectrum (15 eV) shows peaks at m/e (relative intensity) 234 (9, M⁺ − AcOH), 225 (11), 192 (12), 164 (17), 136 (69), 108 (76), 107 (60), 95 (100), 80 (44), 70 (40).

1,5-Bis(acetoxymethyl)tricyclo[2.1.0.0²,⁵]pentan-3-one (XII). A solution of 0.195 g (0.008 mol) of diazo ketone (IX) in 10 mL of ethanol-free chloroform was added dropwise to a stirring solution of 0.004 g (0.009 mmole) of dirhodium tetraacetate in 10 mL of ethanol-free chloroform at 59 °C under a nitrogen atmosphere. When the addition was complete, the green reaction mixture was stirred for 0.5 h at 60 °C and then allowed to cool to 25 °C. The solvent was removed, yielding a brown oil. Chromatography on 25 g of CC7 silica gel with 2:1 hexane/ethyl acetate as the elutant yielded 0.080 g of ketone XII as white crystals: mp 56–57 °C; R_f 0.37 (2:1 hexane–ethyl acetate). Recrystallization from ether gave 0.064 g (37%) of tricyclic ketone XII as long thick needles, mp 57–58 °C.

The proton NMR spectrum (CCl₄) of XII showed a four-proton acetoxymethyl singlet at δ 4.93, a two-proton bridgehead methine singlet at δ 2.16, and a six-proton acetate methyl singlet at δ 2.02. The carbon-13 NMR spectrum (CDCl₃) showed a bridge carbonyl singlet at 181.4 ppm and an acetate carbonyl quartet (^2J = 3.7 Hz) at 170.49 ppm, an acetoxymethyl triplet (^1J = 152.6 Hz) at 55.49 ppm, a bridgehead methine doublet of doublets (^1J = 190.5 Hz and ^4J = 14.7 Hz) at 43.01 ppm, an acetate methyl quartet (^1J = 129.8 Hz) at 20.79 ppm, and a quarternary bridge carbon singlet at 15.33 ppm, relative to CDCl₃ (77.06 ppm) as an internal standard. The infrared spectrum (CCl₄) showed carbonyl absorption at 1795 and 1751 cm⁻¹. The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 224 (2.8, M⁺), 165 (2.8, M⁺ − OAc), 164 (1.7, M⁺ − HOAc), 154 (7.8), 140 (13), 137 (10), 122 (29), 108 (29), 95 (10), 94 (68), 66 (26); exact mass calcd for C₁₁H₁₂O₅ 224.0685, found 224.0685; calcd for C₉H₈O₃ 164.0473, found 164.0474. Anal. Calcd for C₁₁H₁₂O₅: C, 58.98; H, 5.39. Found: C, 58.59; H, 5.35.

1,5-Bis(hydroxymethyl)tricyclo[2.1.0.0²,⁵]pentan-3-one (XIII). To a solution of 0.314 g (0.0024 mol) of ketone (XII) in 10 mL of absolute ethanol was added 0.774 g (0.0056 mol) of anhydrous potassium carbonate at 0 °C. The suspension was stirred for 14 h at 25 °C and then filtered, and the solvent was removed. The resulting oil was chromatographed on 20 g of silica gel with 10:1 ethyl acetate–methanol as the elutant, yielding 0.134 g (68%) of the XIII as a white solid: mp 38–39 °C; R_f 0.45 (10:1 ethyl acetate–methanol). Recrystallization from ether gave clear needles, mp 39–40 °C.

The proton NMR spectrum (acetone-d₆) of XIII shows a two-proton bridgehead methine singlet at δ 2.15, a broad two-proton hydroxyl peak at δ 4.25, and a four-proton hydroxymethyl singlet at δ 4.57. The infrared spectrum (CCl₄) showed bands at 3600 (m, OH), 3500–3350 (m, OH), and 1780 cm⁻¹ (s, C=O). The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 140 (6, M⁺), 110 (10), 94 (12, M⁺ − CO − OH₂), 66 (100); exact mass calcd for C₆H₇O₂ 111.0446, found 111.0446. The partially coupled carbon-13 NMR spectrum (CDCl₃) showed a ketone carbonyl singlet at δ 185.05, a hydroxymethyl carbon triplet at δ 54.32, a methine carbon doublet of doublets at δ 41.32, and a quarternary carbon singlet at δ 18.19.

In an early reaction, which did not proceed to completion, the monoacetate XIV was isolated as an oil, following elution with

ethyl acetate during chromatography on silica gel.

The NMR spectrum (CDCl$_3$) of the monoacetate XIV showed a three-proton acetate methyl singlet at δ 2.07, a two-proton bridgehead methine singlet at δ 2.27, a one-proton hydroxyl singlet at δ 2.85, a two-proton hydroxymethyl singlet at δ 4.59, and a two-proton acetoxymethyl singlet at δ 5.08. The infrared spectrum of XIV showed hydroxyl group absorption at 3620 and 3520 cm^{-1} (broad, hydrogen bonded) together with carbonyl absorption at 1783 and 1740 cm^{-1}.

1,5-Bis(acetoxymethyl)-3,3-diethoxytricyclo[2.1.0.0^{2,5}]-pentane (XVa). To a solution of 0.343 g (0.0015 mol) of ketone diacetate XII and 17 mg (0.089 mmol) of *p*-toluenesulfonic acid monohydrate in 15 mL of absolute ethanol, was added 2.1 mL (0.017 mol) of triethyl orthoformate at 0 °C. After the mixture was stirred 10 h at 0 °C, the reaction was quenched with 50 μL of Hunig's base. The solvent was removed, leaving a light yellow oil which was triturated with five 2-mL portions of pentane. The pentane solution was filtered and evaporated. This yielded 0.446 g (99%) of a clear oil which crystallized in the freezer, mp 38–39 °C. Crystallization from pentane gave pure ketal, mp 45–46 °C.

The proton NMR spectrum (CDCl$_3$) of XVa showed a four-proton acetoxymethyl singlet at δ 4.88, a four-proton ether methylene quartet at δ 3.47 (*J* = 7.07 Hz), a two-proton methine singlet at δ 2.40, a six-proton acetate methyl singlet at δ 2.10, and a six-proton methyl triplet at δ 1.20 (*J* = 7.07 Hz). The infrared spectrum (CDCl$_3$) showed a band at 1730 cm^{-1} (s, acetate carbonyl). The mass spectrum at 15 eV showed peaks at *m/e* (relative intensity) 298 (0.5, M$^+$), 253 (7, M$^+$ – OEt), 239 (32, M$^+$ – OAc), 169 (21), 151 (52), 139 (24), 123 (100, M$^+$ – (EtO)$_2$C – CH$_2$OAc), and 95 (25); exact mass calcd for C$_{15}$H$_{22}$O$_6$ 298.1416, found 298.1420; calcd for C$_{13}$H$_{19}$O$_4$ 239.1283, found 239.1281. The fully coupled carbon-13 NMR spectrum (CDCl$_3$) showed an acetate carbonyl carbon at δ 171.52, a quaternary ketal carbon singlet at δ 112.08, an ether methylene carbon triplet at δ 59.53 (*J* = 141.76 Hz), an acetoxymethyl methylene carbon triplet at δ 58.34 (*J* = 150.62 Hz), a methine carbon doublet of doublets at δ 34.75 (^1J = 185.0 Hz, ^3J = 10.83 Hz), a quaternary carbon singlet at δ 20.75, an acetate methyl carbon quartet at δ 20.66 (*J* = 128.96 Hz), and a methyl carbon quartet at δ 15.19 (*J* = 126 Hz). Anal. Calcd for C$_{15}$H$_{22}$O$_6$: C, 60.38; H, 7.45. Found: C, 60.39; H, 7.14.

1,5-Bis(hydroxymethyl)-3,3-diethoxytricyclo[2.1.0.0^{2,5}]-pentane (XVIa). To a stirred solution of 0.796 g (0.0027 mol) of ketal diacetate XVa in 20 mL of absolute ethanol was added 1.624 g (0.013 mol) of anhydrous potassium carbonate at room temperature. The yellow suspension was stirred for 13 h and then diluted with 20 mL of pentane. Filtration through a pad of Celite and solvent removal yielded the crude diol as a yellow oil. The oil was taken up in 10 mL of anhydrous ethyl ether and filtered through a pad of Celite, and the solvent was removed, yielding 0.572 g (99%) of a clear oil. This oil is suitable for further use, or it can be chromatographed on 25 g of silica gel by eluting with ethyl acetate to give pure diol (*R$_f$* 0.60, 4:1 ethyl acetate–methanol).

The proton NMR spectrum (CDCl$_3$) of XVIa showed a four-proton hydroxymethyl singlet at δ 4.53, a four-proton ether methylene quartet at δ 3.50 (*J* = 6.98 Hz), a two-proton hydroxyl singlet at δ 2.68, a two-proton methine singlet at δ 2.39, and a six-proton methyl triplet at δ 1.21 (*J* = 6.98 Hz). The infrared spectrum (CCl$_4$) showed bands at 3555–3100 cm^{-1} (s, OH). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 169 (8, M$^+$ – OEt), 111 (23), 95 (47), and 94 (45); exact mass calcd for C$_{11}$H$_{18}$O$_4$ 214.1205, found 214.1206. The carbon-13 NMR spectrum (acetone-*d$_6$*) showed a quaternary ketal carbon singlet at δ 111.34, an ether methylene carbon triplet at δ 58.97 (*J* = 138.96 Hz), a hydroxymethyl carbon triplet at δ 54.84 (*J* = 145.33 Hz), a methine carbon doublet of doublets at δ 32.70 (*J* = 173.34, 10.5 Hz), a quaternary carbon singlet at δ 22.17, and a methyl carbon quartet at δ 14.83 (*J* = 125.22 Hz).

1′,5′-Bis(acetoxymethyl)spiro[1,3-dioxolane-2,3′-tricyclo[2.1.0.0^{2,5}]pentane] (XVb). 1,5-Bis(acetoxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (XII; 0.51 g, 0.23 mmol) was treated with *p*-toluenesulfonic acid monohydrate (0.005 g, 0.03 mmole) under an inert atmosphere. The mixture was cooled to −4 °C with an ice–salt bath, and ethylene glycol (1.0 mL) was added followed by triethyl orthoformate (0.314 g, 2 mmol). The stirred reaction mixture warmed to 22 °C over a 4.5-h period. Saturated sodium bicarbonate (25 mL) was added, and the solution was extracted

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Table I. Fractional Coordinates of the Carbon and Oxygen Atoms (× 10^4) and of the Hydrogen Atoms (× 10^3) for 1

atom	*x/a*	*y/b*	*z/c*
C1	4015 (3)	1285 (1)	9942 (1)
C2	2325 (3)	1166 (1)	9009 (1)
C3	2565 (3)	2172 (1)	9465 (1)
C4	3676 (3)	1971 (1)	8616 (1)
C5	5568 (3)	1605 (1)	9340 (1)
C6	7421 (2)	1607 (1)	9414 (1)
C7	777 (3)	351 (1)	8625 (2)
O8	1909 (2)	−565 (1)	8404 (1)
C9	765 (4)	−1440 (1)	8181 (1)
O10	−1078 (3)	−1460 (1)	8149 (1)
C11	2064 (5)	−2350 (2)	8009 (2)
C12	1480 (4)	3050 (2)	9844 (2)
C13	3079 (2)	3756 (1)	10335 (1)
C14	2515 (4)	4455 (2)	10957 (2)
O15	800 (3)	4491 (1)	11125 (1)
C16	4317 (9)	5122 (4)	11422 (4)
H1	405 (3)	98 (1)	1057 (1)
H4	345 (3)	229 (1)	800 (1)
H7A	−12 (3)	58 (1)	800 (1)
H7B	−5 (3)	14 (1)	911 (1)
H11A	358 (5)	−224 (2)	816 (2)
H11B	178 (4)	−252 (2)	730 (2)
H11C	182 (5)	−296 (3)	831 (2)
H12A	62 (4)	344 (1)	930 (2)
H12B	76 (3)	278 (1)	1031 (1)
H16A	411 (8)	564 (3)	1101 (3)
H16B	422 (6)	542 (3)	1195 (3)
H16C	553 (5)	501 (3)	1122 (3)

with four 100-mL portions of diethyl ether. The ether layers were combined, concentrated, treated with Nuchar C-190 N, and filtered through Super Cel, and the solvent was removed, yielding 0.199 g of pale yellow oil. The oil was chromatographed on 10 g of Silicar CC-7 Special and eluted with 50:50 ethyl acetate–hexane; 20-mL aliquots were collected. Fraction 3–5 were combined to yield 0.057 g of clear oil after solvent removal. The oil was dissolved in diethyl ether–hexane and seeded. After the oil had been allowed to stand at room temperature for 1 day, 0.038 g (61%) of beautiful white prisms (mp 84–85 °C) were deposited.

The NMR spectrum (CCl$_4$) showed an eight-proton methine and acetate methyl singlet at δ 2.02, a four-proton ethylenedioxy singlet at δ 3.76, and a four-proton acetoxymethyl singlet at δ 4.82. The infrared spectrum showed an acetate carbonyl at 1740 cm^{-1}. The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 268 (5, M$^+$), 210 (15), 209 (100, M$^+$ – OAc), 184 (13), 183 (13), 168 (13), 167 (100), 166 (94), 165 (26), 154 (21), 150 (81), 140 (13), 139 (32), 138 (34), 123 (38), 122 (11), 110 (15), 95 (34), 94 (55), 87 (65), and 73 (90); exact mass calcd for C$_{11}$H$_{13}$O$_4$ 209.0814, found 209.0816. The fully coupled carbon-13 NMR spectrum (acetone-*d$_6$*) showed a quaternary ketal carbon singlet at δ 111.34, an ether methylene carbon triplet at δ 58.97 (*J* = 138.96 Hz), a hydroxymethyl carbon triplet at δ 54.85 (*J* = 145.33 Hz), a methine carbon doublet of doublets at δ 32.70 (*J* = 173.34, 10.5 Hz), a quaternary carbon singlet at δ 22.17, and a methyl carbon quartet at δ 14.83 (*J* = 125.22 Hz).

1′,5′-Bis(hydroxymethyl)spiro[1,3-dioxolane-2,3′-tricyclo[2.1.0.0^{2,5}]pentane] (XVIb). Compound XVb (0.036 g, 0.13 mmol) was dissolved in ethanol (5.0 mL) and cooled in ice. Potassium carbonate (0.038 g, 0.27 mmol) was added. The stirred reaction mixture was allowed to warm to 24 °C and was stirred for 7.5 h. Hexane (5 mL) was added to precipitate potassium bicarbonate, and the mixture was filtered. The solvent was removed, yielding 0.024 g (97%) of colorless oil.

The NMR spectrum (CDCl$_3$) showed a two-proton methine singlet at δ 2.21, a two-proton broad hydroxyl singlet at δ 2.76, a four-proton ethylenedioxy singlet at δ 3.88, and a four-proton hydroxymethyl singlet at δ 4.55. The infrared spectrum (CDCl$_3$) showed hydroxyl group absorption at 3615 and 3420 cm^{-1}.

Crystallographic Data and X-ray Structure Analysis of 1,5-Bis(acetoxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (XII). The cell dimensions were determined by least-squares methods from 63 high-order reflections (2θ > 42°) measured with Mo K$_\alpha$

radiation on a computer-controlled diffractometer (Siemens AED). Crystal data: $a = 6.5497$ (5), $b = 12.654$ (1), $c = 13.887$ (2) Å; $\beta = 101.902$ (8); $V = 1126.2$ Å³; space group $P2_1/c$; $Z = 4$; $M_r = 224.22$; $d_c = 1.32$ g cm⁻³. With a crystal of the dimensions 0.27 × 0.30 × 0.57 mm³ mounted on the diffractometer 2711 independent reflections were recorded for sin $\theta/\lambda \leq 0.664$ Å⁻¹ with graphite-monochromated Mo Kα radiation. A total of 1086 reflections were treated as unobserved $(F_o{}^4/[\sigma(F_o{}^2)]^2 < 7)$. Lorentz and polarization corrections were applied, and absorption effects were neglected.

The crystal structure was solved by direct methods with the program MULTAN.[9] The positions of the hydrogen atoms were calculated according to geometrical requirements or were found by a difference Fourier synthesis. After several least-squares refinement cycles in the full-matrix procedure with isotropic temperature parameters for the hydrogen atoms and anisotropic temperature parameters for the carbon and oxygen atoms we obtained a final R values of 0.05 (excluding unobserved reflections) and 0.06 (unobserved reflections included); $R = \sum |kF_o - |F_c||/\sum kF_o$. In the last refinement cycle 297 unobserved reflections were included ($|F_c| > kF_o$). Three of the strongest reflections affected by extinction were assigned zero weight. The final

positional coordinates of the atoms are listed in Table I. Further information is given in the supplementary material. The scattering factors were obtained from the literature.[10] The computations were carried out in the computer center (IBM 370/168) at the University of Heidelberg.

Registry No. I, 1573-17-7; II, 82903-05-7; III, 82903-06-8; IV, 82903-07-9; V, 78998-60-4; VI, 78998-59-1; VII, 78998-61-5; VIII, 82903-08-0; IX, 78998-62-6; X, 82903-09-1; XI, 82917-45-1; XII, 78998-58-0; XIII, 81710-08-9; XIV, 82903-10-4; XVa, 82903-11-5; XVb, 82903-12-6; XVIa, 82903-13-7; XVIb, 82903-14-8; ethyl diazoacetate, 623-73-4; dirhodium(II) tetraacetate, 15956-28-2; *tert*-butyl diazoacetate, 35059-50-8; oxalyl bromide, 15219-34-8.

Supplementary Material Available: Thermal parameters for compound XII and a table of some short intramolecular contacts (2 pages). Ordering information is given on any current masthead page.

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Photocleavage of Diarylnitrosamines in Neutral Media

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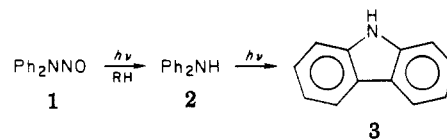
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N-Nitrosodiphenylamine, *N*-nitroso(2-nitrophenyl)phenylamine, *N*-nitroso(3-methylphenyl)phenylamine, and *N*-nitrosocarbazole were irradiated in degassed neutral solution to give the corresponding diarylamine as the initial photoproduct. The effects of changing solvents, concentrations, and substituents and of adding catalysts were examined. Quantum yield studies, sensitization work, and ESR studies were used to study the mechanism of this photolysis.

The early reports[5] of low photoreactivity for nitrosamines in the absence of acid catalysts led to extensive studies on the acid-catalyzed photoreactions.[6] Although a few compounds[7-9] were reported to be photolabile in the absence of acid, there was no study of the efficiency of the uncatalyzed photoreactions. We began investigating the efficiency of the uncatalyzed photoreactions of diarylnitrosamines in order to clarify their mechanisms and to perhaps better understand the relationships between the excited states in these molecules. We note that *N*-nitrosodiphenylamine (1) has been found to be only weakly carcinogenic[10a,b] after extensive studies.[10c]

Exploratory Photochemical Results

Our initial studies[11] showed that 1 was converted to diphenylamine (2) on Pyrex-filtered irradiation in deoxy-

genated neutral solution (see Table I) as had been previously reported.[7] The production of 2 showed a clear solvent dependence in that more of the amine 2 was produced in solvents of better hydrogen-donating ability. Catalytic amounts of both thiol and proton acid also increased the amine production. Extended irradiation gave the expected secondary photoproduct carbazole (3).[12] If

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