Treatment of this compound with 5 *N* hydrochloric acid in ethanol yielded a red, crystalline product, mp >300°.

Anal. Calcd for empirical formula $C_{20}H_{14}NO_3$: C, 75.94; H, 4.46; N, 4.43; O, 15.18. Found: C, 75.81; H, 4.44; N, 4.35; O, 15.24.

Registry No.—**1a**, 23265-38-5; **1b**, 23265-39-6; **1b** formate, 23282-25-9; **1c**, 23265-40-9; **2a**, 23265-41-0; **2a** formate, 23282-31-7; **2a** perchlorate, 23265-43-2; **2b**, 23265-42-1; **2c**, 23282-32-8; **2d**, 23265-44-3; **2e**, 23265-45-4; **3a**, 23265-46-5; **3b**, 23265-47-6; **3c**, 23265-48-7.

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Inter- and Intramolecular Cyclization of Bisdiazo Ketones. The Formation of the Novel 3,3′-Spirobi(bicyclo[3.1.0]hexane)-2,2′-dione System

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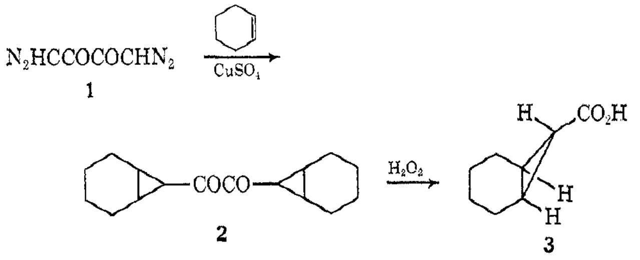
Two examples of double addition of bisdiazo ketones to olefinic bonds are described. Addition of 1,4-bisdiazo-2,3-butanedione (**1**) to cyclohexene afforded the *exo*-di(7-norcaryl)ethanedione (**2**). Catalytic decomposition of bisdiazo ketone **8** yielded the isomeric spiro diketones **10** and **11**. Nmr spectral properties and some reactions of this novel spiro system are discussed.

α-Ketocarbenes generated by the copper-catalyzed decomposition of diazo ketones have been found to react with olefins to produce cyclopropanes. Both intermolecular[1-3] and intramolecular[4-13] additions have been reported.

Recently we initiated the study of the corresponding reactions of bisdiazo ketones which do not appear to have been investigated. In the present paper we describe two cases in which double addition of intermediate bisketocarbenes to olefinic bonds occurred.

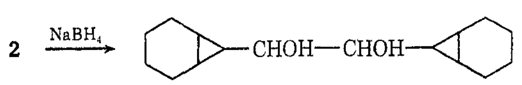
Decomposition of 1,4-bisdiazo-2,3-butanedione (**1**)[14] in boiling cyclohexene in the presence of anhydrous copper sulfate afforded the *exo*-di(7-norcaryl)ethanedione **2** in low yield.



The presence of an α-diketone system was demonstrated by formation of the corresponding quinoxaline derivative. The low carbonyl frequency (1680 cm^{-1}) observed in the infrared spectrum of **2** indicates a significant conjugative overlap between the cyclopropane rings and the adjacent carbonyl groups, presumably enhanced by a preferred geometry of the molecule with respect to the pertinent groups. Conjugative ability of the electron-rich cyclopropane ring has been observed for many years by infrared and ultraviolet spectroscopy.[15,16]

The *exo* configuration was proved by oxidation of **2** with alkaline hydrogen peroxide, affording the *exo* isomer of norcarane-7-carboxylic acid (**3**).[17,18] Thus the configuration agrees with previous experience concerning copper-catalyzed decomposition of ethyl diazoacetate in the presence of olefins. Here also addition favored the formation of the less hindered *exo* product.[17-20]

Nmr data also support the *exo* configuration. It has been shown[21] that in α-cyclopropylcarbonyl compounds the *cis* ring protons with respect to the carbonyl group are shifted to low field. This should obtain in all *exo* isomers of a norcaryl system adjacent to a carbonyl group. (In the *exo* isomer the carbonyl group is located *trans* to the cyclohexane ring.) Indeed, for **2** and **3** no proton resonance has been observed at δ values lower than 1.17 and 1.10 ppm, respectively. Similarly, in methyl norcaryl ketone **4** no proton resonance has



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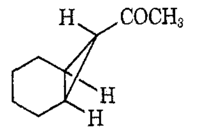

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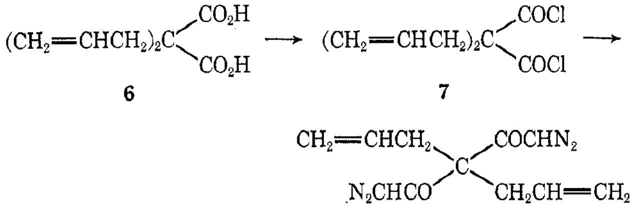
been reported at δ values less than 1 ppm.[22] Sodium borohydride reduction of **2** afforded the diol **5**, the nmr spectrum of which exhibited a broad six-proton multiplet at high field (δ 0.4–1.0 ppm) as expected for the cyclopropyl protons once the "carbonyl effect" present in **2** has been removed.

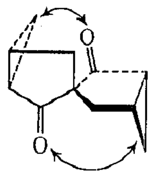
In order to study the case of intramolecular cyclization, the bisdiazo ketone **8** was prepared by the addition of diazomethane to diallyl malonyl chloride **7** obtained from the corresponding acid **6** with oxalyl chloride.



$(CH_2{=}CHCH_2)_2C(CO_2H)_2 \longrightarrow (CH_2{=}CHCH_2)_2C(COCl)_2 \longrightarrow (CH_2{=}CHCH_2)(N_2CHCO)C(COCHN_2)(CH_2CH{=}CH_2)$

6　**7**　**8**

The decomposition of the bisdiazo ketone **8** was then investigated under varying conditions of temperature, solvent, and catalyst. In each case two isomeric crystalline products, A (mp 154°) and B (mp 118°), were isolated, representing two of the three theoretically possible stereoisomers, **9**, **10**, and **11**. The distribution of isomers A and B in the crude reaction mixture was analyzed by glpc and is summarized in Table I.



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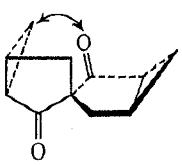

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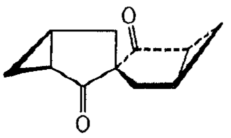

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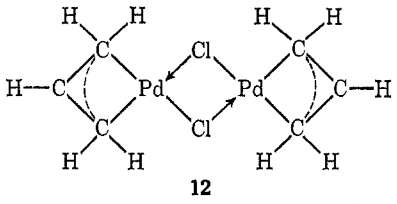
TABLE I

DECOMPOSITION OF 8 UNDER DIFFERENT CONDITIONS

Catalyst	Temp, °C	Solvent	A + B, %	A, %	B, %
$CuSO_4$	100	Dioxane	15	67	33
Pd complex	5–15	Dioxane	35	86	14
Pd complex	5–15	THF	24	85	15
Pd complex	5–15	Ether	22	85	15
Pd complex	5–15	Benzene	23	74	26

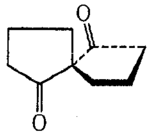
The higher yields obtained by using the π-allylic palladium chloride complex **12**[23] instead of $CuSO_4$ are presumably due to the milder conditions necessary to effect decomposition with this complex,[24] lessening concurrent polymer formation.



12

Although the infrared and ultraviolet spectra of the spiro diketones A and B are similar the striking difference observed in their nmr spectra permitted establishment of their relative configuration.

Both compounds showed two distinct carbonyl stretching bands in their infrared spectra (see Experimental Section). In the ultraviolet region both A and B had a maximum at 280 nm (ε 96 and 127, respectively). Similarly, a high ε value (121) was found for the n → π* transition band of the spiro ketone **13**[25] in contrast to the low ε values of 13, 22, and 24 observed for cyclopentanone and two related monoketones, **14** and **15**. The effect was discussed by Cram for the diketone **13**,[25] where the π orbitals of two apparently nonconjugated chromophores appear to interact because they are held in rigid proximity, although orthogonal to one another. Considering the ε values of 57 and 46 reported for the bicyclo ketones **16**[26a] and **17**,[26b] the values of 96 for compound A and 127 for B appear to be normal (double the value for a single carbonyl chromophore). Consequently, our spiro ketones do not obey the "spiro conjugation" effect discussed recently for interactions observed between p-orbital systems (olefins and oxygen or nitrogen lone-pair electrons) in numerous spiro compounds.[27] The already existing conjugation in the α-cyclopropyl ketone system presumably overhelms this spiro effect.



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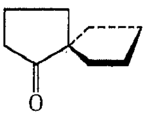

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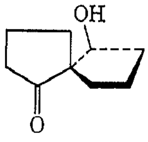

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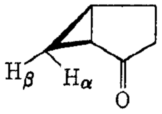

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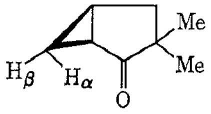

17

It is important to recognize the difference in the symmetry properties of **9**, **10**, and **11**. Since **10** lacks any symmetry element, it is asymmetric. Both **9** and **11** have one twofold symmetry axis (C_2) and are therefore dissymmetric. This symmetry difference must be reflected also in the corresponding nmr spectra, permitting structural assignments to be made for the isomers actually isolated, A and B, provided that one of them is **10**. Indeed, the spectra of both A and B exhibited four distinct multiplets, integrated for an even-numbered distribution of protons only in the case of A but not in that of B (*vide infra*). Isomer B must therefore be the asymmetric **10**. In order to decide whether the major product A is **9** or **11**, its nmr spectrum was compared with those of the bicyclo[3.1.0]hexan-2-ones **16** and **17**, in which H_α and H_β have been reported to resonate as multiplets at δ 0.8–1.3 and 0.6–1.5 ppm, respectively.[27] In the spectrum of A there were four distinct multiplets centered at δ 0.72 (2 H), 1.22 (2 H), 1.98 (6 H), and 2.54 ppm (2 H). The two upfield multiplets, corresponding to the geminal cyclopropyl protons, appear in a range similar to that of the corresponding methylene signals in both model compounds **16** and **17**. This close accord would be expected only for structure **11**, where the geminal cyclopropyl protons

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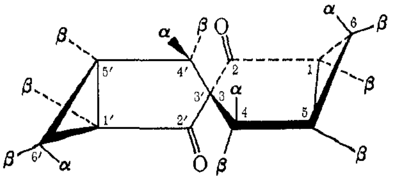
TABLE II

COUPLING CONSTANTS[a] FOR SOME 3,3′-SPIROBI(BICYCLO[3.1.0]HEXANE) DERIVATIVES

Compd	$J_{2\beta,1\beta}$	$J_{2'\beta,1'\beta}$	$J_{4\beta,5\beta}$	$J_{4\alpha,4\beta}$	$J_{6\beta,4\beta}$	$J_{6\beta,1\beta}$	$J_{6\alpha,5\beta}$ $J_{6\alpha,1\beta}$	$J_{6\alpha,6\beta}$
10	...	...	5.5	13.0	1.5	...	4.5	3.5
11	...	...	5.5	13.0	1.5	...	4.5	3.5
22	4.5	5.0	5.0	13.0	...	8.0	5.0	5.0
23	5.0	...	5.5	13.0	...	...	...	...
34	...	5.0	5.5	13.0	1.5	...	...	...

[a] Reported in hertz.

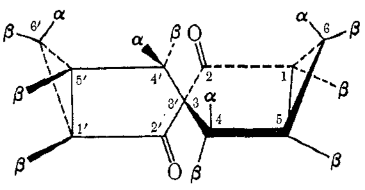
would not experience any additional anisotropic effects of the distant carbonyl group. (Compare, for example, the relative locations of $H_{6\alpha}$ and the $C_{2'}$ carbonyl group in I.) On the other hand, both *endo* methylene protons of the cyclopropyl rings in **9** are located in close proximity to the carbonyl groups (see **9**), and their chemical shifts would be expected to differ significantly from those observed in the model compounds **16** and **17**. These assumptions are confirmed by the nmr spectrum of the asymmetric isomer B (**10**), which indeed combines the characteristic configurations of both **9** and **11** (*vide infra*).



I

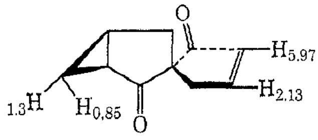
The assignment of the geminal cyclopropyl protons was made on the basis of the order $J_{cis} > J_{trans}$, established for vicinal coupling constants in cyclopropane derivatives.[19,28–30] Consequently, the narrower multiplet ($W_{1/2}$ = 13 Hz) at highest field (δ 0.72 ppm) represents the magnetically equivalent *endo* protons $H_{6\alpha}$ and $H_{6'\alpha}$ (see I) appearing as a six-line pattern present in an unsymmetrical triplet. The broader multiplet ($W_{1/2}$ = 24 Hz) centered at δ 1.22 ppm corresponds to the resonance of the *exo* protons $H_{6\beta}$ and $H_{6'\beta}$. An unsymmetrical doublet of quartets represents the protons $H_{4\beta}$ and $H_{4'\beta}$, with a splitting pattern corresponding to coupling of $H_{4\beta}$ with the protons $H_{4\alpha}$, $H_{5\beta}$, and $H_{6\beta}$. (Owing to the symmetry of the molecule, $H_{4'\beta}$ is similarly coupled to $H_{4'\alpha}$, $H_{5'\beta}$, and $H_{6'\beta}$.) The coupling constants obtained from the spectrum and confirmed by double-irradiation experiments are summarized in Table II.

The nmr spectrum of the isomer B consisted of four multiplets centered at δ 0.89 (1 H), 1.20 (2 H), 2.00 (8 H), and 2.96 ppm (1 H). The integration, compared with the integration values of isomer A (*vide supra*), suggests that isomer B has the asymmetric configuration shown in II. Here, in contrast to the symmetric molecule (I), one cyclopropyl group is inverted. This change in the relative configuration of one cyclopropane ring eliminates the anisotropic shielding effect of this ring[31–34] on $H_{4\beta}$ which exists in the symmetric molecule. This proton, now affected only by the anisotropic effect of the $C_{2'}$ carbonyl group, is shifted downfield (from 2.54 to 2.96 ppm). Simultaneously, $H_{4'\beta}$, located in the shielding volume above the plane of both cyclopropyl rings, undergoes an upfield shift into the area of the complex multiplet centered at δ 2.00 ppm. The *endo* proton $H_{6'\alpha}$, affected by the C_2 carbonyl group, is shifted downfield, leaving a one-proton multiplet at highest field (δ 0.89 ppm) corresponding to $H_{6\alpha}$.



II

A different product, **18**, has been isolated from the reaction mixture of the copper-catalyzed decomposition of **8** in hydrocarbons (hexane, cyclohexane, or benzene) rather than dioxane. The structure of **18** was substantiated by elemental analysis and spectral data. The relative configuration of the cyclopropane ring was determined from the chemical shifts of the geminal cyclopropyl protons, which appeared in the range similar to that for the corresponding methylene signals of **11**. For the relative configuration of the methyl group and the vinylic hydrogen, support has been found in nmr data reported for compounds **18** and **19**.[35]



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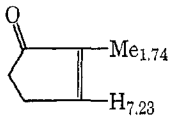

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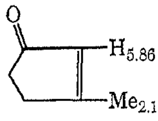

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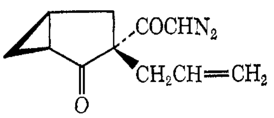
Compound **18** cannot result from rearrangement of A or B, since, when both were refluxed in benzene in the presence of copper sulfate, work-up of the solutions gave only recovered starting material. A monocyclized intermediate such as **21** may serve as a common precursor for all three compounds, **10**, **11**, and **18**.



21

Reduction of **11** with sodium borohydride afforded a mixture of neutral and acidic fractions. The neutral fraction consisted of two of the three stereochemically possible diols **22**, **23**, and **24** separated by chromatography or, alternatively, by preparative glpc of the corresponding trimethylsilyl ethers followed by hydrolysis.

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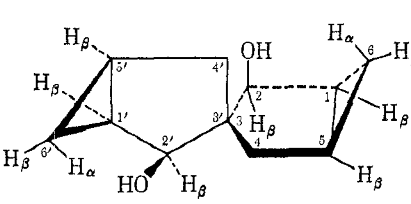
Metal hydride reduction of conjugated cyclopropyl ketones has been shown to give (in over 90% yield) the isomer in which the hydroxyl and cyclopropane groups are *cis*.[36,37]

The two isomeric diols were obtained in a ratio of *ca.* 85:15, and it is reasonable to assume that in the major product (mp 171°) each set of hydroxyl group and cyclopropyl ring are in the *cis* orientation, as depicted in **22**. This assumption was confirmed by the nmr data. The presence of a clearly resolved doublet in pyridine-d_5 at δ 4.88 ppm (2 H, J = 4.5 Hz) attributed to the tertiary protons $H_{2\beta}$ and $H_{2'\beta}$ supports symmetrical disposition of the two hydroxyl groups about the C_2 axis, a feature absent in **23**. The splitting of the absorption of these hydrogens is reasonably explained as resulting from coupling with the *cis* protons $H_{1\beta}$ and $H_{1'\beta}$. Although the hydroxyls in **24** are also symmetrically disposed and are thus magnetically equivalent, $H_{2\alpha}$ and $H_{2'\alpha}$ would be expected to appear as a singlet. This expectation is based on the observation in models that the relevant dihedral angles ($H_{2\alpha}$–C–C–$H_{1\beta}$ and $H_{2'\alpha}$–C–C–$H_{1'\beta}$) approximate 90° and therefore no spin–spin coupling should be observed.[38]



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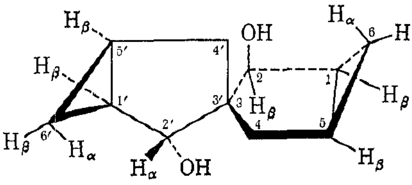

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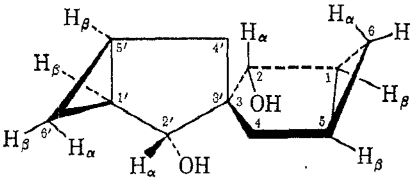

24

The asymmetric structure **23** has been assigned to the minor component, a liquid diol characterized as its bis-*p*-nitrobenzoate. Its nmr spectrum in $CDCl_3$ exhibited a one-proton doublet at δ 4.82 ppm (J = 5 Hz) and a one-proton singlet at δ 3.77 ppm corresponding to $H_{2\beta}$ and $H_{2'\alpha}$, respectively. Both protons differ in chemical shifts from that of the corresponding tertiary protons in the diol **22**. Presumably, this difference may be accounted for by the $H_{2\beta}$ resonance undergoing a paramagnetic shift owing to the neighboring $C_{2'\beta}$ hydroxyl;[36,39,40] the $H_{2'\alpha}$ proton lies in the shielding area of the neighboring cyclopropyl group.[41] The lesser symmetry of **23** is further supported by the fact that, in contradiction to the magnetic equivalence of $H_{4\beta}$ and $H_{4'\beta}$ in **22**, in **23** only $H_{4'\beta}$ is affected by the C_2 hydroxyl group, which resonated separately at δ 2.40 ppm (quartet, 1 H, $J_{4'\beta,4'\alpha}$ = 13 Hz, $J_{4'\beta,5'\beta}$ = 5 Hz). The $H_{4\beta}$ resonance was shifted to higher field into a seven-proton multiplet at δ 1.1–1.8 ppm ($H_{1\beta}$, $H_{1'\beta}$, $H_{5\beta}$, $H_{5'\beta}$, $H_{4\alpha}$, $H_{4'\alpha}$, and $H_{4\beta}$).

The infrared spectra of the two diastereoisomeric diols **22** and **23** in the OH stretching region furnished further support for the above configurational assignment. The infrared spectrum of **22** exhibited a sharp band at 3595 cm^{-1} and a broad one at 3415 cm^{-1}. At low concentration the broad (intermolecular) band disappears. The diol **23** also showed two infrared bands, at 3570 and 3470 cm^{-1}, but they remain relatively unchanged even at low concentration. The geometry of **22**, with *trans* hydroxyl groups, permits no intramolecular hydrogen bonding. In the isomer **23**, however, intramolecular bonding may exist owing to the relative proximity of the hydroxyl groups.[42,43]

The acidic fraction, obtained as a by-product, consisted of a mixture of two isomeric hydroxy acids, one of them present as a minor component but detectable in the nmr spectrum of the crude acidic fraction. The major acidic component (mp 131°) was separated by chromatography on silica gel.

The formation of hydroxy acids may be explained by a two-step reaction, in which the basic sodium borohydride first cleaves the β diketone **11**. Whether the enolate anion **25** is further reduced or first converted into epimeric keto acids **26** and **27** by proton abstraction has not been investigated. This uncertainty in the mechanism requires consideration of four isomeric hydroxy acids, **28–31**, as potential reaction products.

Configurational assignment for the actually isolated hydroxy acid was attempted by considering the presence of a one-proton resonance at δ 4.05 ppm in the nmr spectrum owing to the proton α to the hydroxyl group. Table III summarizes the expected splitting pattern of this signal in the four hydroxy acids **28–31**. Dihedral angles were measured in Dreiding models and coupling constants were derived from the Karplus curve.[38] Since a boat conformation is preferred for bicyclo[3.1.0]hexan-2-ol and -3-ol,[44,45] our analysis also uses this conformation.

Although this analysis is only approximate, the presence of an ill-resolved multiplet, centered at δ 4.05 ppm in the nmr spectrum of the hydroxy acid (mp 131°), together with the well-established fact of obtention of *cis* hydroxyl groups in metal hydride reductions of conjugated cyclopropyl ketones,[36,37] it is suggested that the hydroxy acid be either **28** or **30**. Clear-cut differentiation between these two configurations, however, was not possible, since the data provide insufficient evidence concerning the configuration of the side chain.

One keto acid (**26** or **27**) was isolated in 95% yield

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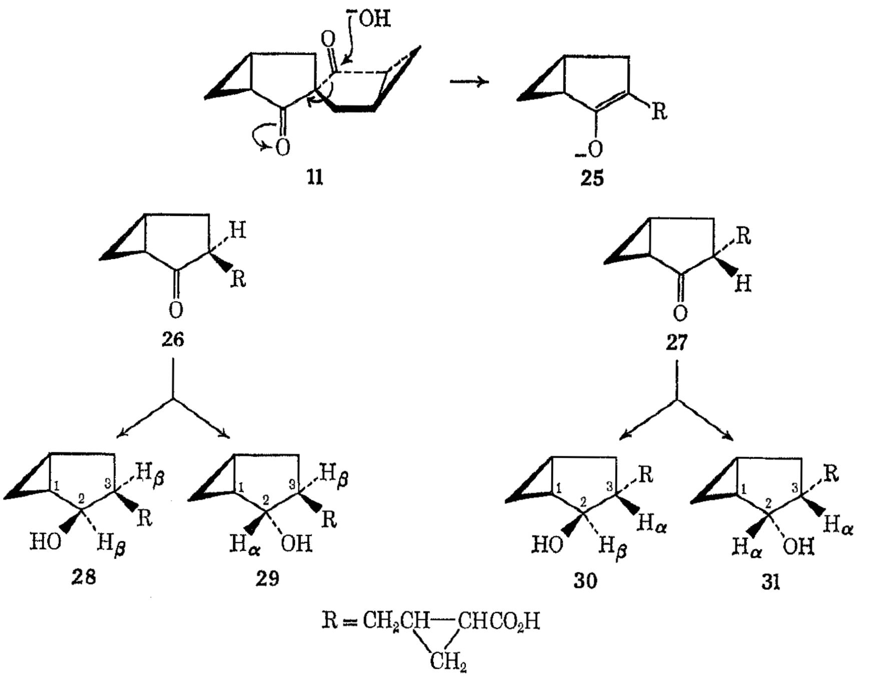


Table III

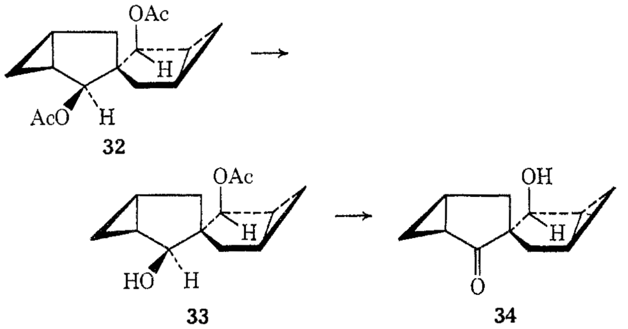
Estimated Coupling Constants[a] from Measured Dihedral Angles in Bicyclo[3.1.0]hexan-2-ol Derivatives

Compd	Coupled protons	Dihedral angle, deg	J	Expected H_2 resonance
28	$H_{1\beta}$, $H_{2\beta}$	45	4	Quartet
	$H_{2\beta}$, $H_{3\beta}$	30	6	
29	$H_{1\beta}$, $H_{2\alpha}$	75	0	Singlet
	$H_{2\alpha}$, $H_{3\beta}$	90	0	
30	$H_{1\beta}$, $H_{2\beta}$	45	4	Quartet
	$H_{2\beta}$, $H_{3\alpha}$	150	7	
31	$H_{1\beta}$, $H_{2\alpha}$	75	0	Doublet
	$H_{2\alpha}$, $H_{3\alpha}$	30	6	

[a] Reported in hertz.

when the diketone **11** was refluxed with sodium hydroxide followed by acidification. Presumably under these conditions the thermodynamically more stable isomer is formed. Its methyl ester showed a single sharp peak upon glpc on two different columns. This keto acid, on reduction with sodium borohydride, yielded the same hydroxy acid as was obtained from the diketone **11** as described above.

The diacetate **32** of the diol **22** served as a starting material for preparing the ketol **34**. Partial hydrolysis of the diacetate gave, besides unchanged diacetate and diol, the monoacetate **33**, which on oxidation with chromic acid followed by hydrolysis furnished the ketol **34**. Its structure was confirmed by analysis and spectroscopic methods.



Experimental Section

All melting points were taken in capillaries and are uncorrected. The ir spectra were determined on a Perkin-Elmer Infracord and the uv spectra on a Perkin-Elmer 137 or on a Cary 14 spectrophotometer. The nmr spectra were recorded either on a Varian A-60 or on a Varian HA-100 spectrometer in $CDCl_3$ solution if not otherwise stated, using TMS as internal standard. Gas chromatographic analyses were done on a F & M Model 810 or on a Aerograph HY-FI Model 600D gas chromatograph.

exo-**Di(7-norcaryl)ethanedione** (**2**).—A stirred mixture of 1,4-bisdiazo-2,3-butanedione 1[14] (3.58 g), redistilled dry cyclohexene (*ca.* 700 ml), and anhydrous copper sulfate (20 g) was heated under reflux under N_2 until the ir bands characteristic for the diazo ketone disappeared (*ca.* 15 hr). The mixture was cooled and filtered from copper sulfate and polymeric materials, and the solvent was removed. The oily residue (4.8 g) was chromatographed on a column of Florisil (60–100 mesh, 100 g). Elution with hexane and crystallization from MeOH gave the ethanedione **2** (0.35 g): mp 130–131°; ir ($CHCl_3$) 1678 cm^{-1}; uv max (MeOH) 240 mμ (ε 9700).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.0; H, 9.0. Found: C, 77.8; H, 9.0.

A sample of diketone **2**, on treatment with *o*-phenylenediamine, yielded **2,3-di(7-norcaryl)quinoxaline**, mp 72° (from EtOH).

Anal. Calcd for $C_{22}H_{26}N_2$: C, 83.0; H, 8.2; N, 8.8. Found: C, 82.4; H, 8.5; N, 8.6.

exo-**Norcarane-7-carboxylic Acid** (**3**).—A mixture of the diketone **2** (0.13 g), MeOH (20 ml), aqueous NaOH (15%, 15 ml), and H_2O_2 (30%, 9 ml) was kept at room temperature overnight. Excess H_2O_2 was decomposed with $FeSO_4$, and the solution was acidified with cold, aqueous HCl and extracted with ether. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed. The crude acid was recrystallized from pentane (0.10 g), mp 96–97.5° (lit.[18] mp 96.5°).

exo-**Di(7-norcaryl)ethanediol** (**5**).—To a solution of diketone **2** (0.25 g) in EtOH (30 ml), sodium borohydride (0.04 g) was added in small portions and the mixture was kept at room temperature overnight. Ethanol was then removed under reduced pressure, water was added, and the mixture was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water until neutral reaction, dried, and evaporated. The crude diol (0.23 g) was purified by recrystallization from hexane, mp 99–100°.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.8. Found: C, 76.6; H, 10.8.

1,5-Bisdiazo-3,3-diallyl-2,4-pentanedione (8).—To a magnetically stirred and ice-cooled mixture of diallyl malonic acid (36.8 g), dry benzene (200 ml), and anhydrous pyridine (1 ml) was added dropwise a solution of freshly distilled oxalyl chloride (80 ml) in dry benzene (80 ml). The addition was regulated according to rate of gas evolution. After the addition was completed, the ice bath was removed and the mixture was slowly heated to 40° and kept at this temperature for 2 hr and then at 60° for an additional 2 hr. Excess oxalyl chloride and benzene were removed and the residue was washed three times with 150 ml of dry ether. For characterization the solvent was removed from a small sample and the ir spectrum of the residual oil was taken in dry CCl_4, ν_{max} 1800 (-COCl) and 1650 cm^{-1} ($CH_2{=}CH$-).

The combined etheral extracts were added dropwise under cooling and swirling to an etheral diazomethane solution (prepared from 160 g of nitrosomethylurea). After standing for 1 hr the solution was filtered and concentrated until the product started to crystallize. The bisdiazo ketone was isolated by suction filtration and recrystallized from benzene-cyclohexane (1:1): mp 81–82°; ir ($CHCl_3$) 2110, 1645, and 1630 cm^{-1}; nmr δ 2.6 (d, 4), 5.5 (s, 2), and 4.9–5.8 ppm (m, 6).

Anal. Calcd for $C_{11}H_{12}O_2N_4$: C, 56.9; H, 5.2; N, 24.1. Found: C, 57.3; H, 5.2; N, 23.8.

Decomposition of Bisdiazo Ketone 8 with CuSO$_4$.—A stirred mixture of diazo ketone **8** (6.0 g), redistilled dry cyclohexane (600 ml), and anhydrous $CuSO_4$ (12 g) was heated under reflux under N_2 until the ir bands characteristic for the diazo ketone disappeared (*ca.* 40 hr). The mixture was cooled and filtered from $CuSO_4$, and polymeric material and the solvent were removed. The dark, oily residue was purified by column chromatography on Florisil (60–100 mesh, 150 g). Elution with hexane–benzene (1:1) gave crude **18**, which was recrystallized from *i*-PrOH (0.28 g): mp 135°; ir ($CHCl_3$) 1730, 1696, and 1628 cm^{-1}; uv max (MeOH) 225 mμ (ϵ 10,200); nmr δ 5.97 (vinylic proton) and 2.13 ppm (methyl).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 75.0; H, 6.9.

Decomposition of Bisdiazo Ketone 8 with Complex 12.—To an ice-cold solution of 1,5-bisdiazo-3,3-diallyl-2,4-pentanedione (30 g) in absolute ether (3 l.), the Pd complex **12**[23] (0.3 g) was added. Vigorous gas evolution started immediately. After the reaction subsided, the ice bath was removed and the mixture was stirred overnight at room temperature. After filtration and concentration of the solution, crude crystalline diketone **11** was obtained (3.28 g), purified by recrystallization from *i*-PrOH: mp 154°; ir ($CHCl_3$) 1736 and 1706 cm^{-1}; uv max (MeOH) 280 mμ (ϵ 96).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 74.9; H, 7.0.

Removal of the solvents of the combined mother liquors gave a crude oil which was chromatographed on a column of Florisil (60–100 mesh). Elution with hexane–benzene (4:1) gave diketone **10** (0.68 g). The analytical sample was obtained by recrystallization from *i*-PrOH: mp 118°; ir ($CHCl_3$) 1734 and 1710 cm^{-1}; uv max (MeOH) 281 mμ (ϵ 127).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 74.8; H, 7.0.

Elution with hexane–benzene (1:1) gave an additional amount (1.03 g) of isomer **11**, mp 154°.

Reduction of Diketone 11 with Sodium Borohydride.—To a solution of diketone **11** (2.0 g) in *i*-PrOH (150 ml) kept at 40°, sodium borohydride (2.0 g) was added. The mixture was left at room temperature overnight, the solvent was removed, and water was added. The solution was neutralized (pH 7) with diluted HCl and extracted with $CHCl_3$. After the usual work-up, an oil was obtained which on trituration with $CHCl_3$ gave the crystalline diol **22** (1.07 g). The analytical sample was obtained by recrystallization from acetonitrile: mp 171°; ir (CCl_4) 3595 and 3415 cm^{-1}; the broad band at 3415 cm^{-1} disappears at a concentration of 2 × 10^{-3} mol/l.; mass spectrum *m/e* 162 ($M^+ - H_2O$).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.3; H, 9.0. Found: C, 73.0; H, 8.8.

The bis-*p*-nitrobenzoate melted at 271° ($CHCl_3$).

Anal. Calcd for $C_{25}H_{22}N_2O_8$: C, 62.8; H, 4.6; N, 5.9. Found: C, 62.4; H, 5.0; N, 6.2.

Removal of the solvents ($CHCl_3$ and *i*-PrOH) of the combined mother liquors gave a thick oil which was chromatographed on a column of basic Alumina (Merck). Elution with C_6H_6-$CHCl_3$ (1:1) gave an additional amount (0.38 g) of diol **22**; C_6H_6-$CHCl_3$ (1:2) eluted the isomeric oily diol **23** (0.26 g). For purification it was rechromatographed on neutral Alumina (Merck), ir (CCl_4) 3570 and 3470 cm^{-1}. Both peaks remain relatively unchanged at a concentration of 4 × 10^{-4} mol/l., mass spectrum *m/e* 162 ($M^+ - H_2O$).

The bis-*p*-nitrobenzoate melted at 182–183° (CH_3CN).

Anal. Calcd for $C_{25}H_{22}N_2O_8$: C, 62.8; H, 4.6; N, 5.9. Found: C, 62.7; H, 4.7; N, 5.8.

The aqueous layer from the first $CHCl_3$ extraction was acidified with cold, diluted HCl to pH 2 and extracted again with $CHCl_3$. After the organic layer had been dried (Na_2SO_4) the solvent was removed and the nmr spectrum of the crude residue (0.26 g) was taken. The presence of a multiplet at δ 4.05 ppm, together with a doublet at δ 4.40 ppm, indicated the crude residue to be a mixture of two hydroxy acids. Trituration with benzene and recrystallization of the crude crystalline product from benzene–chlorform gave pure hydroxy acid, mp 131°. Alternatively, the crude acidic mixture was chromatographed on silica gel (28–200 mesh, Davison Chemical), and elution with $CHCl_3$ afforded an oil which crystallized on standing. Recrystallization from benzene–chlorform gave the hydroxy acid, mp 131°. The nmr spectrum exhibited a one-proton multiplet at δ 4.05 ppm, but the doublet observed in the spectrum of the crude acid at δ 4.40 ppm was absent.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.3; H, 8.2. Found: C, 66.9; H, 8.3.

In an alternative procedure a portion of the neutral fraction obtained from the sodium borohydride reduction described above was converted into a mixture of the corresponding trimethylsilyl ethers using a modification[46] of a standard method.[47] The ether mixture was analysed by glpc on a 6 ft × 0.25 in. column packed with SE-30 (3%) on 80–100 mesh Chromosorb W at a column temperature of 155°. Three peaks with relative area of 86:8:6 were observed. The major fraction was collected and hydrolyzed for 5 min with boiling MeOH. The product, mp 171°, was identical with the symmetrical diol **22** (*vide supra*). Glpc comparison of the product with relative area intensity 8 with the trimethylsilyl ether of diol **23** showed the identity of these two compounds. The product corresponding to the third peak was not investigated.

Alkaline Cleavage of Diketone 11.—A solution of diketone **11** (0.12 g) in a mixture of EtOH (4 ml) and NaOH (6 *N*, 1 ml) was heated under reflux for 30 min. After removal of the alcohol under reduced pressure and acidification with cold, diluted HCl to pH 3, a keto acid **26** or **27** precipitated (0.12 g). Recrystallization from benzene gave the analytical sample: mp 123°; ir 1712 cm^{-1}; mass spectrum *m/e* 194 (M^+).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 67.8; H, 7.4.

Reduction of the Keto Acid.—A solution of the keto acid (0.28 g), mp 123°, in *i*-PrOH (28 ml) at 40° was treated with sodium borohydride (0.28 g), and the mixture was left at room temperature for 20 hr. After removal of the solvent, water was added and the acidified (pH 2) solution was extracted with $CHCl_3$. After the usual work-up, an oil (0.27 g) was obtained, which on trituration with benzene and recrystallization from benzene–chloroform gave the hydroxy acid, mp 131°, identical with that described above.

Acetylation of Diol 22.—A mixture of diol **22** (0.70 g), anhydrous pyridine (5 ml), and acetic anhydride (2.5 ml) was heated at 100° for 50 min and then cooled, and all the volatile compounds were removed under reduced pressure. Sublimation of the residue at 80° (0.05 mm) afforded diacetate **32** (0.92 g). The analytical sample was obtained by recrystallization from pentane, mp 93–94°; in the nmr spectrum the protons α to the acetoxy groups resonated at δ 5.20 ppm (d, 2 H).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.2; H, 7.6. Found: C, 68.2; H, 7.5.

Preparation of Ketol 34.—Diacetate **32** (0.80 g) in dioxane (20 ml), water (8 ml), and 40% aqueous dioxan (18.7 ml) containing KOH (9 mg/ml) was refluxed for 30 min. The addition of phenolphthalein showed that this time was required for the consumption of the KOH. The cooled solution was concentrated to dryness under high vacuum, water was added, and the

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mixture was extracted with $CHCl_3$. The crude material (*ca.* 0.70 g) obtained from the dried $CHCl_3$ solution was chromatographed on neutral alumina (50 g, Merck). Elution with benzene gave unchanged diacetate (0.21 g), identified by melting point and mixture melting point. Elution with benzene–chloroform (9:1) afforded the oily monoacetate **33** (0.36 g), characterized as its *p*-nitrobenzoate, mp 119–121° (from methylcyclohexane).

Anal. Calcd for $C_{20}H_{21}O_6N$: C, 64.7; H, 5.7. Found: C, 64.3; H, 5.7.

Elution with $CHCl_3$ gave diol **22** (0.08 g), identified by melting point and mixture melting point.

The crude oily monoacetate (0.28 g) in "Analar R" acetone (20 ml) was treated with Jones solution[48] (0.6 ml) at 0°. After the solution had been stirred for 5 min, excess oxidant was destroyed by adding methanol (2 ml). After the solution had been neutralized ($NaHCO_3$) and filtered, the solvent was removed and the residue was extracted with CH_2Cl_2. The crude keto acetate (0.28 g), obtained from the dried CH_2Cl_2 solution, in dioxane (8 ml), and 40% aqueous dioxane (7.5 ml) containing KOH (9 mg/ml) was refluxed for 30 min (negative phenolphthalein reaction). The cooled solution was concentrated to dryness under high vacuum, water was added, and the mixture was extracted with $CHCl_3$. After the usual work-up, a thick oil (0.2 g) was isolated which solidified on standing. Trituration with ether and recrystallization from methylcyclohexane afforded the ketol **34**, mp 124–125°.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.2; H, 7.9.

Registry No—**2**, 23346-32-9; **5**, 23346-30-7; **8**, 23346-31-8; **10**, 23353-38-0; **11**, 23353-39-1; **18**, 23353-40-4; **22**, 23353-41-5; **22** bis-*p*-nitrobenzoate, 23353-42-6; **23**, 23353-43-7; **23** bis-*p*-nitrobenzoate, 23353-44-8; **26**, 23359-84-4; **27**, 23353-45-9; **28**, 23353-46-0; **29**, 23359-83-3; **30**, 23353-34-6; **31**, 23353-35-7; **32**, 23353-36-8; **33** *p*-nitrobenzoate, 23353-37-9; **34**, 23353-56-2; 2,3-di(7-norcaryl)quinoxaline, 23346-33-0.

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Organometallic Reaction Mechanisms. IV. The Mechanism of Ketone Reduction by Aluminum Alkyls

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A product analysis, kinetic study, and Hammett study of the reaction of triisobutylaluminum with benzophenone has been carried out in diethyl ether solvent. There is no significant participation of the second alkyl group in triisobutylaluminum reduction of benzophenone up to 94% yield of benzhydrol, which is the only product formed in the reaction. The kinetic data shows a well-behaved second-order reaction, first order in aluminum alkyl and first order in ketone. The formation of a complex between the ketone and aluminum alkyl was observed spectroscopically. Accumulation of kinetic data at several temperatures provided a linear Arrhenius plot, which allowed for calculation of activation parameters ($\Delta S^* = -10.1$ eu, $\Delta H^* = 15.8$ kcal/mol, and $\Delta G^* = 18.8$ kcal/mol). A ρ value of +0.362 was determined from a Hammett study, which indicates that the rate-determining step involves nucleophilic attack of the carbonyl group by the aluminum alkyl. All of the accumulated data is consistent with a two-step mechanism in which the first step involves a fast equilibrium to form a complex according to the equation $(i\text{-}C_4H_9)_3Al + (C_6H_5)_2C{=}O \rightleftarrows (i\text{-}C_4H_9)_3Al\cdot O{=}C(C_6H_5)_2$. The second step is rate determining and is consistent with a cyclic intramolecular β-hydrogen attack at the carbonyl group (eq 15).

Organoaluminum compounds react with carbonyl compounds in a similar way to Grignard reagents to give products of either addition, reduction, or enolization reactions or any combination of these reactions. Although the reaction of triethylaluminum with carbonyl compounds produces a mixture of addition and reduction products,[1] the primary reaction of organoaluminum compounds with branched alkyls is reduction.[2] For example, the reaction of triisobutylaluminum with carbonyl compounds is very characteristic in that no addition product is formed with most carbonyl compounds.[1b,c,3]

Recent successes in kinetic studies on the addition reaction of trimethylaluminum with benzophenone in benzene[4] and diethyl ether[5] and the reduction reaction of *t*-butylmagnesium compounds with di-*t*-butyl ketone in tetrahydrofuran[6] have encouraged the study of the mechanism of the reduction reaction of trialkylaluminum compounds with carbonyl compounds by kinetic methods. An ideal system for this study involves the reaction of triisobutylaluminum with benzophenone, since only the formation of reduction product in high yield has been reported.[1b,c] Since this reaction was reported too fast to follow kinetically in benzene,[1c] kinetic studies on this reaction were carried out in diethyl ether, a solvent which provided a convenient reaction rate for kinetic measurements. Furthermore, since triisobutylaluminum is monomeric in diethyl ether[7] and the reaction of the first alkyl group is reported to be much more rapid than that of the second alkyl group, this particular aluminum alkyl should provide the least complicated kinetic data.

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