ride salt formation was omitted in this instance. The yields and physical constants of the products are given in Table I.

Registry No.—Sodium dicyanamide, 1934-75-4.

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On the Reaction of α-Diazo Ketones with *m*-Chloroperoxybenzoic Acid

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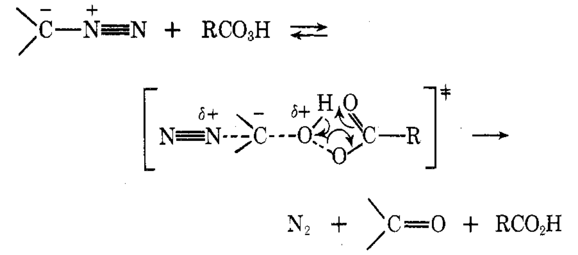
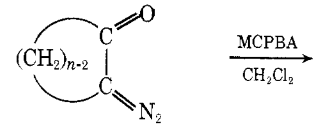
In a previous paper[2] we have shown that diazodiphenylmethane $Ph_2C{=}N_2$ and substituted diazodiphenylmethanes react with peroxy acids to afford the corresponding diaryl ketones in high yield.

On the basis of kinetic evidence, a reaction mechanism was proposed which involves attack by the nucleophilic carbon atom of the diazo group on the peroxide O–O bond.[2]

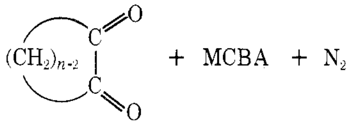


(1)

Therefore, at variance with what was found for carboxylic acids,[3] it appears that peroxy acids transfer "electropositive" oxygen and not H^+ to the diazo group. We now report that α-diketones are produced in the reaction of some cyclic α-diazo ketones **1a–e** and of acyclic 3-diazo-2-butanone $CH_3CN_2COCH_3$ (**2**) with *m*-chloroperoxybenzoic acid (MCPBA) in the mole ratio of 1:1, in CH_2Cl_2 at 25° (eq 2).



1a, $n = 6$; **1b**, $n = 8$; **1c**, $n = 9$;
1d, $n = 10$; **1e**, $n = 12$



(2)

Yields and kinetic data are shown in Table I. Under the conditions given, the yields of the corresponding α-diketones were essentially quantitative from **1a**, **1d**, **1e**, and **2**. The yields were considerably less with **1b** and **1c** as starting materials, but substantial amounts of suberic and azelaic anhydride, respectively, appeared in the reaction mixtures. These anhydrides undoubtedly arise from the initially formed α-diketones in a subsequent competitive reaction with MCPBA. It is known, in fact, that α-diketones react with peroxy acids in organic solvents[4] and with HO_2^- in aqueous media[5] to yield the corresponding anhydrides, presumably *via* a Baeyer–Villiger type mechanism.[6]

Table I
Yields and Rates of Reaction of Some α-Diazo Ketones with *m*-Chloroperoxybenzoic Acid in Methylene Chloride at 25°

Compd	% yield of[a] α-diketone	10^2k_2,[b] M^{-1} sec^{-1}
1a	99 (glc)	16.8
1b	40 (isol.)[c]	20.5
1c	35 (glc)[c]	30.0
1c	30 (isol.)[c]	30.0
1d	95 (isol.)	12.0
1e	92 (isol.)	4.27
2	96 (glc)	5.52

[a] As determined (±5%) by glc analysis or by isolating (ref 2) and weighing the α-diketone, after reacting the diazo compound with MCPBA in equimolar amounts. [b] Evaluated (±3%) as $k_1/[\mathrm{MCPBA}]_0$, from pseudo-first-order kinetic experiments. [c] Ir analysis of reaction mixtures and comparison with authentic samples showed that the α-diketone produced was accompanied by 25–30% of the parent anhydride, while 20–25% of the α-diazo ketone starting material had remained unreacted.

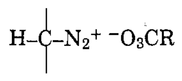
Indeed, in independent experiments we have verified that 1,2-cyclononanedione, 1,2-cyclooctanedione, and also 2,3-butanedione (biacetyl) all give the corresponding anhydrides in nearly quantitative yields (glc, ir) when allowed to react with MCPBA in CH_2Cl_2.

The absence of rearrangement[7,8] or transannular reaction products[9] in detectable amounts from the oxidation of cyclic α-diazo ketones suggest that mechanisms involving carbene or cation intermediates[2] are unlikely.

In the series of medium-ring α-diazo ketones examined the rates pass through a maximum for $n = 9$. However, the overall differences in rate are small and might easily be ascribed to transition-state and/or ground-state conformational effects. A recent dnmr study of **2** has revealed that this compound exists in $CDCl_3$ solutions as an equilibrium mixture of rapidly interconverting s-*E* (transoid) and s-*Z* (cisoid) conformers;[10] at 25° the ratio [s-*E*]/[s-*Z*] is *ca.* 3.3.[10] This finding is in good agreement with the observed dipole moment of **2** (μ = 2.45 D) and the calculated dipole moments of its s-*Z* and s-*E* forms (3.9 and 1.7 D, respectively).[11]

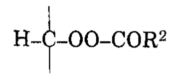
We have measured the dipole moments of cyclic **1a** and **1e** and found μ = 3.9 and 2.15 D, respectively. Thus, in the series of medium-ring α-diazo ketones **1a–e** one apparently proceeds from a situation where the cisoid form is highly prevalent over the transoid to the opposite. Kinetic data, however, show that **1e** react with MCPBA at nearly the same rate as **2,** and only *ca.* four times slower than **1a.** This is not surprising since cisoid and transoid forms of α-diazo ketones would be expected to display similar nucleophilic reactivity in the absence of severe steric hindrance and/or conformational effects. In fact, coplanarity of the $O{=}C{-}\bar{C}{-}\overset{+}{N}{\equiv}N$ moiety is required for maximum pπ delocalization; therefore, the fractional negative charge on carbon part of the CNN fragment should be nearly the same for undistorted *E* and *Z* forms.[12]

It is interesting to compare the trend of relative rates with ring size for the oxidation of cyclic α-diazo ketones by MCPBA with the pattern observed for reactions involving other medium-ring compounds (Figure 1). At variance with reactions I and II,[13] which represent rather clear-cut examples of, respectively, sp³ → sp² and sp² → sp³ rehybridization at the reaction center, the MCPBA oxidation of medium-ring α-diazo ketones is little influenced by ring size. The pattern resembles that observed for the CsCHA-catalyzed tritio deprotonation of cycloalkanes (reaction III).[14] Thus, for both reaction III and the MCPBA oxidation of α-diazo ketones (reaction IV), transition states should have conformations only little different from ground states.[15] In any case, mechanisms involving formation of intermediate



$$H{-}\overset{|}{\underset{|}{C}}{-}N_2^{+}\ {}^{-}O_3CR$$

ion pairs and of unstable peroxy esters



$$H{-}\overset{|}{\underset{|}{C}}{-}OO{-}COR^2$$

should be dismissed as this would involve sp² → sp³ rehybridization at the reaction center.

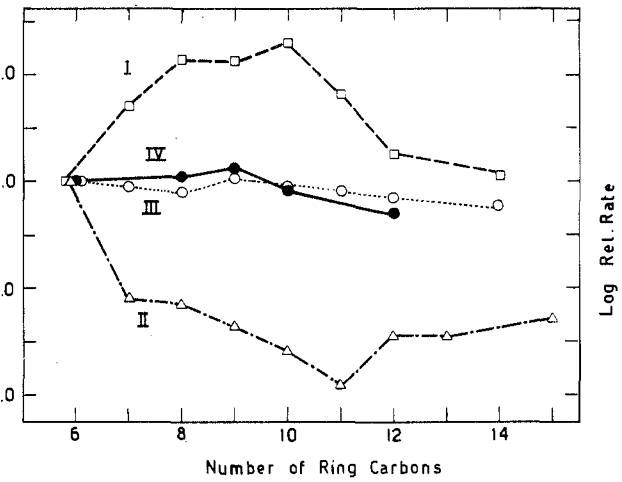


Figure 1. Comparison of relative rate pattern with ring size for the acetolysis of cycloalkyl tosylates (I), borohydride reduction of cycloalkanones (II), and CsCHA catalyzed tritio deprotonation of cycloalkanes (III) with the oxidation of 2-diazocycloalkanones by MCPBA (IV).

Experimental Section

General. Melting and boiling points were not corrected. Nmr spectra were recorded on a Bruker HFX-10 spectrometer (90 MHz); chemical shifts were measured downfield from TMS internal standard. Ir spectra were taken on a Perkin-Elmer Model IR-457 instrument and uv–visible spectra on a Cary 15 spectrophotometer. Dipole moments were determined by the method of Hedestrand;[16] dielectric constants of solutions were measured at 20° by using a heterodyne apparatus at a frequency of 1 MHz. Molar refractions were calculated from Vogel's increments.[11] Analytical glc was performed on a Varian-Aerograph Model 1520 instrument equipped with tc detector by using a 6 ft × ⅛ inch o.d. column (5% FFAP on Chromosorb G AW-DMCS, 80–100 mesh).

Materials. The α-diazo ketones and the α-diketones employed were prepared according to reported methods.[8,17–19] Their physical constants and ir spectra agreed with data reported in the literature. **2-Diazocyclohexanone:** bp 50–51° (0.3 mm); vis max (CH_2Cl_2) 400 nm (ϵ 20); nmr ($CDCl_3$) δ 2.74 (m, 2, $O{=}CCH_2$), 2.30 (m, 2, $N_2{=}CCH_2$), and 1.78 ppm (m, 4, CH_2); μ (CCl_4) 3.90 D, ${}_{\infty}P_2$ 347.3 and R_D 32.6 cm³ mol⁻¹; ir (CCl_4) 2090 ($C{=}N_2$) and 1640 cm⁻¹ ($C{=}O$). **2-Diazocycloctanone:** oil; vis max (CH_2Cl_2) 395 nm (ϵ 16); nmr ($CDCl_3$) δ 2.53 (m, 4, $={CCH_2}$) and 1.62 ppm (m, 8, CH_2); ir (CCl_4) 2085 ($C{=}N_2$) and 1635 cm⁻¹ ($C{=}O$). **2-Diazocyclononanone:** oil; vis max (CH_2Cl_2) 395 nm (ϵ 16); nmr ($CDCl_3$) δ 2.50 (m, 4, $={CCH_2}$) and 1.60 ppm (m, 10, CH_2); ir (CCl_4) 2085 ($C{=}N_2$) and 1630 cm⁻¹ ($C{=}O$). **2-Diazocyclodecanone:** mp 58–59° (lit.[8] 56.5–57°); vis max (CH_2Cl_2) 390 nm (ϵ 25); nmr ($CDCl_3$) δ 2.76–2.42 (m, 4, $={CCH_2}$) and 1.49 ppm (broad, 12, CH_2); ir (CCl_4) 2085 ($C{=}N_2$) and 1645 cm⁻¹ ($C{=}O$). **2-Diazocyclododecanone:** mp 43–44° (lit.[17] 42–43°); vis max (CH_2Cl_2) 410 nm (ϵ 28); nmr ($CDCl_3$) δ 2.69 (m, 2, $O{=}CCH_2$), 2.22 (m, 2, $N_2{=}CCH_2$), and 1.30 ppm (broad, 16, CH_2); μ (CCl_4) 2.15 D, ${}_{\infty}P_2$ 158.3 and R_D 60.6 cm³ mol⁻¹; ir (CCl_4) 2065 ($C{=}N_2$) and 1640 cm⁻¹ ($C{=}O$). **3-Diazo-2-butanone:** bp 35–40° (12 mm);[20] vis max (CH_2Cl_2) 415 nm (ϵ 8); nmr ($CDCl_3$) δ 2.20 (broad, s, 3, $O{=}CCH_3$) and 1.97 ppm (broad, s, 3, $N_2{=}CCH_3$);[10] ir (CCl_4) 2070 ($C{=}N_2$) and 1645 cm⁻¹ ($C{=}O$). Commercial (Schuchardt) *m* **-chloroperoxybenzoic acid** was purified following a given method[21] to a purity of 99%+ (iodometric assay), mp 92–93°.[21]

Kinetics. Kinetic runs were performed under pseudo-first-order conditions with $[MCPBA]_0$ being usually from 10- to 20-fold excess over the initial concentration of the diazo ketone. The change of absorbance was monitored in the great majority of cases at or near the wavelength of maximum absorption in the visible for each diazo compound.[2] A Gilford Model 2400 recording spectrophotometer equipped with thermostatic cell holder (±0.5°) was employed. Rate constant values which appear in Table I are averages from three or more independent runs.

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Registry No.—**1a**, 3242-56-6; **1b**, 14088-64-3; **1c**, 18208-20-5; **1d**, 18208-23-6; **1e**, 14078-83-2; **2**, 14088-58-5; *m*-chloroperoxybenzoic acid, 937-14-4.

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Transition Metal Catalyzed Conjugate Methylation of α,β-Unsaturated Ketones by Trimethylaluminum and Lithium Tetramethylaluminate

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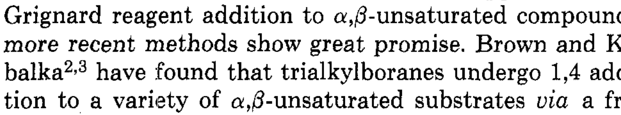
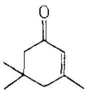
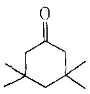
Recently there has been an increased interest in methods for effecting 1,4 addition to α,β-unsaturated systems.[1] In addition to lithium alkylcuprate and copper-catalyzed Grignard reagent addition to α,β-unsaturated compounds, more recent methods show great promise. Brown and Kabalka[2,3] have found that trialkylboranes undergo 1,4 addition to a variety of α,β-unsaturated substrates *via* a free radical chain process. More recently Kabalka and Daley[4] found that trialkylaluminum compounds exhibit analogous behavior when photolyzed at −78° or in the presence of catalytic amounts of oxygen, and were able to demonstrate the intermediacy of free radical species. Because of our interest in the area of transition metal catalyzed reactions of main group organometallic reagents, we were particularly interested in the recent report by Mole, *et al.*,[5] concerning nickel catalyzed conjugate addition of trimethylaluminum to α,β-unsaturated ketones. It would appear that this



$$(CH_3)_3Al + R\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[H^+]{H_2O} R\underset{CH_3}{\overset{H}{C}}CH_2\overset{O}{\overset{\|}{C}}R' \quad (1)$$

method represents a convenient and potentially economic route to 1,4-addition products, particularly if the reaction is stereoselective. In an attempt to determine the stereoselectivity of this reaction and in addition to determine the applicability of this method to 1,4-conjugate addition to prostaglandin precursors, we synthesized 4-methyl-2-cyclopentenone, 4-acetoxy-2-cyclopentenone, and 4-methyl-2-cyclohexenone. We wish now to report the results of not only $(CH_3)_3Al$ addition, but also $LiAl(CH_3)_4$ addition to a variety of α,β-unsaturated ketones in order to provide information concerning the scope and stereochemistry of these reactions.

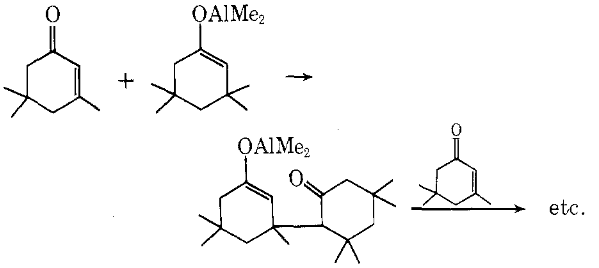
Table I
Reaction of Trimethylaluminum with Isophorone in the Presence of Nickel Acetylacetonate

Time, min	 (mmol)	 (mmol)	Material balance, %
0	1.000	0.000	100
1	0.300	0.680	98
5	0.075	0.838	91
30	0.000	0.845	85
60	0.000	0.863	86
120	0.000	0.850	84

Results and Discussion

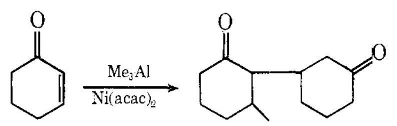
Table I presents data obtained by sequential quenching of aliquots from the reaction of trimethylaluminum with 3,5,5-trimethyl-2-cyclohexenone (isophorone) in the presence of 3.0 mol % nickel acetylacetonate [$Ni(acac)_2$].

Several features of Table I are striking. While Mole, *et al.*,[5] suggest typical reaction times of 18 hr for the reaction of α,β-unsaturated ketones with trimethylaluminum in the presence of $Ni(acac)_2$, our data indicate that methylation is essentially complete in less than 30 min. The only other product formed is polymer and its formation seems to occur only while unreacted isophorone is present. This suggests that the polymer is formed by Michael addition to the aluminum enolate of the product to the α,β-unsaturated ketone according to eq 2. The isolation of 1 after



(2)

nickel acetylacetonate catalyzed addition of trimethylaluminum to 2-cyclohexenone provides additional support for this suggestion.



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(3)

In Table II are listed the results obtained for the catalyzed reaction of trimethylaluminum with isophorone and 2-cyclohexenone. In all cases the starting material was entirely consumed and no other volatile products were formed. It is apparent from the data that ether is the solvent of choice and that cupric acetylacetonate is an effective catalyst. Although Mole[5] suggests that cobalt acetylacetonate was an effective catalyst, in our hands only starting material was recovered after attempted reaction of isophorone with trimethylaluminum in the presence of 3 mol % cobalt acetylacetonate. This result, however, suggests partici-