TABLE I
OXIDATION OF NORBORNENE AT 60° [a]

Product	Mmoles	Mmoles of C_7H_{10}	Mmoles of O_2
Norcamphor + norbornene oxide	1.37	1.37	0.68
Norbornanediol	0.53	0.53	0.53
Unidentified volatiles (3)	0.17	0.17	0.17
CO_2	0.44	...	0.44
Residue[b]	7.32	7.32	8.62
		9.39	10.44

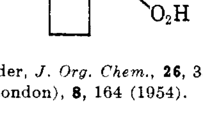
[a] C_7H_{10} (244.8 mmoles) in 20.57 g of benzene, [ABN] = 0.00956 *M*, $[C_7H_{10}]_{60}$ = 4.68 *M*, absorbed 13.8 mmoles of O_2 in 289 min at an average oxygen pressure of 47 psia. The aliquot taken for analysis corresponds to 11.2 mmoles of O_2. [b] Material (971 mg) that analyzed as $C_7H_{10.7}O_{2.34}$ and contained 0.674 mmole of titratable hydroperoxide.

dure of removing the benzene and unreacted norbornene by vacuum distillation; remaining products were separated into volatile and nonvolatile fractions. The volatile fraction was found to contain no hydroperoxide and was analyzed directly by glpc. The residue was analyzed for carbon and hydrogen, with the results shown in Table I.

Clearly the major product of norbornene oxidation is the nonvolatile residue. We suspect that, in addition to some norbornene–oxygen copolymer, derivatives of cyclopentane-1,3-dicarboxaldehyde are present. The subsequent oxidation of this material to peracid accounts for the small peroxide titer and for the oxygen content in excess of the theoretical for the copolymer. We attribute the high hydrogen content of the residue to analytical error. The product analyses in Table I show that none of the norbornene oxidizes by the abstraction mechanism and that no norbornene-1-hydroperoxide is formed. The high reactivity of the olefin toward alkylperoxy radicals must therefore reside in the double bond. Bridging of the cyclohexene ring has thoroughly deactivated the allylic bridgehead hydrogen atoms and increased the reactivity of the double bond by eight- to ninefold.

1,5,9-Cyclododecatriene.—The oxidation of this 1,5-diene was studied briefly in a search for transannular effects like those observed in strong acid treatment.[4] Two experiments were carried out with the undiluted hydrocarbon obtained from Columbia Carbon Co. At 60°, with 257 mmoles of $C_{12}H_{18}$, 0.00963 *M* ABN, and 50–60-psia oxygen, 15.6 mmole oxygen was absorbed in 631 min. The initial rate was 0.0211 mole/l. hr, with a chain length of 51. At 70° with 0.00963 *M* ABN and 50-psia oxygen, the rate was 0.0622 mole/l. hr with a chain length of 37. These rates are one-half to one-third of that found with cyclohexene and about twice that found with cyclododecene. In both experiments strong autocatalysis was observed and iodometric titration indicated that only 52.5% (60° run) of the absorbed oxygen was present as hydroperoxide, a common situation with 1,5-dienes where nontitrable cyclic peroxides are formed.[5] The product is therefore taken to be mainly corresponding to abstractions of allylic hydrogen atoms and intramolecular additions of the resulting peroxy radicals.

$C_{12}H_{18}O_4$,



Removal of the unreacted hydrocarbon from the 70° run followed by exhaustive hydrogenation of the residue gave a mixture of alcohols. Acetylation of the alcohols followed by chromatography indicated five components present, all of approximately equal volatility. Although the exhaustive hydrogenation consumed only 2.73 moles of hydrogen per mole of residue, it is not evident that much transannular ring closure occurred. Conversion of the alcohol mixture to hydrocarbon skeleton by the procedure of Cope and coworkers[6] gave a mixture which is 85–90% cyclododecane. A preliminary shoulder on the main peak of the gas chromatography trace could[7] be bicyclo[4.6.0]-dodecane, but would constitute only 10–15% of the mixture. Thus, little or no transannular carbon–carbon-bond formation occurred at an average oxygen pressure of 50 psia.

Registry No.—Norbornene[2.2.1]bicycloheptene, 498-66-8; 1,5,9-cyclododecatriene, 4904-61-4.

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[4] E. T. Niles and H. R. Snyder, *J. Org. Chem.*, **26**, 330 (1961).

[5] L. Bateman, *Quart. Rev.* (London), **8**, 164 (1954).

[6] A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **84**, 2170 (1962).

[7] An alternate possibility is *n*-dodecane (which arises by reduction of products from oxidative cleavage of one olefin bond of the triene).

Reaction of 2-Carbethoxycycloalkanones with 1,4-Dichloro-2-butene

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In an investigation of methods of preparation of bicyclo[4.3.1]dec-3-en-10-one (Ic), it was observed that sodium ethoxide produces cleavage of 2-carbethoxycyclohexanone while sodium *t*-amylate catalyzes alkylation.[1]

When sodium *t*-amylate was used as the base in the alkylation of 2-carbethoxycycloalkanones of five-, six-, and seven-membered rings with 1,4-dichloro-2-butene, only 2-carbethoxycyclohexanone gave a bicyclic compound, Ia. 2-Carbethoxycyclopentanone and 2-carbethoxycycloheptanone both gave almost entirely polymeric material. Simple alkylation of all three compounds by 1-chloro-4-ethoxy-2-butene was accomplished in the presence of sodium *t*-amylate. When sodium ethoxide was used as the base in the reaction with either 1,4-dichloro-2-butene or 1-chloro-4-ethoxy-2-butene, 2-carbethoxycyclopentanone and 2-carbethoxycyclohexanone[2] both were cleaved and 2-carbethoxycycloheptanone again was alkylated without cleavage.

The structure of the cleavage product in the reaction with 2-carbethoxycyclohexanone, ethyl 6-carbethoxy-10-ethoxy-8-decenoate (II), was indicated by the infrared spectrum, which showed characteristic absorption at 5.75 and 8.50 μ and failed to indicate a carbonyl

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[1] Spiro[4.5]dec-2-en-6-one instead of bicyclo[4.3.1]dec-3-en-10-one was formed by the *t*-amylate-catalyzed reaction between cyclohexanone and 1,4-dichloro-2-butene.

[2] Isolation of some 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclohexanone (III) showed that cleavage of 2-carbethoxycyclohexanone was accompanied by some alkylation without cleavage.

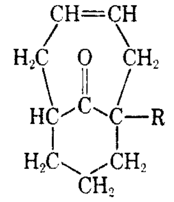
group, and by the nmr spectrum, which accounted for all 30 hydrogens in their assigned positions. Confirmation of the structure was obtained when the same product was obtained with 1-chloro-4-ethoxy-2-butene. The structure of ethyl 5-carbethoxy-9-ethoxy-7-nonenoate, from 2-carbethoxycyclopentanone, was established by its infrared spectrum and from its synthesis by the same two routes.

The structure of 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cycloheptanone was also established when the two alkylations gave the same product. The structures of the corresponding compounds with five- and six-membered rings were obtained from the similarity of their infrared spectra and refractive indices to those of 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)-cycloheptanone.

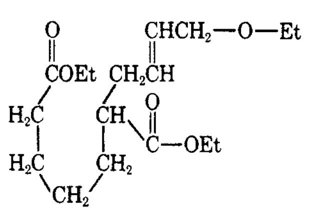
Hydrolysis of II produced α-(δ-valeric acid)-γ-vinyl-γ-valerolactone (IV). The structure of IV was indicated by the infrared absorption at 5.65 μ, characteristic of γ-lactones, and confirmed by the nmr spectrum where the multiplet around 5.5 ppm (relative to tetramethylsilane) characteristic of the vinyl group was particularly important.

Cleavage of β-keto esters by alkoxide has been reported previously[3-5] and the observation that the cleavage is much more likely to occur with ethoxide than with *t*-amylate has been discussed. The stronger and more bulky base favors the Dieckmann condensation by which the β-keto ester is formed[6] without, at the same time, favoring its reversal (cleavage).[5]

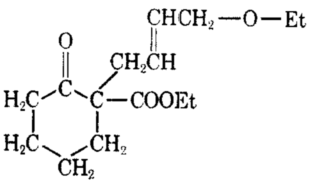
This investigation has shown an important difference in behavior of 2-carbethoxycycloalkanones with five-, six-, and seven-membered rings during alkylation; none of them is readily cleaved by *t*-amylate.[7] With ethoxide the five-membered ring gives only cleavage, the six-membered ring gives mainly cleavage, and the seven-membered ring fails to give any cleavage.



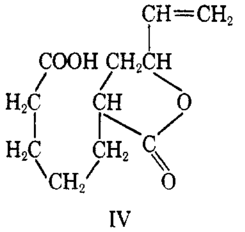
Ia, R = COOEt
b, R = COOH
c, R = H



II



III



IV

Experimental Section

2-Carbethoxycyclopentanone and 2-carbethoxycyclohexanone (Arapahoe Chemicals), 2-carbethoxycycloheptanone and *cis*- and *trans*-1,4-dichloro-2-butene were prepared or purified as described previously.[8,9] 1-Chloro-4-ethoxy-2-butene was prepared in 50.6% yield by alkylation of *trans*-1,4-dichloro-2-butene with sodium ethoxide in ethyl alcohol. A colorless liquid, bp 65–75° (22 mm), n^{24}_{D} 1.4403,[10] was obtained. Ethyl 1-carbethoxy-2-oxocyclohexaneacetate was prepared by the method of Ramirez and Sargent.[11] A colorless liquid, bp 127° (1 mm), n^{24}_{D} 1.4640, whose infrared spectrum agreed with that reported,[12] was obtained.

Ethyl 6-Carbethoxy-10-ethoxy-8-decenoate (II). **A.**—A solution of 170 g (1.0 mole) of 2-carbethoxycyclohexanone in ethanolic sodium ethoxide prepared from 46 g (2.0 moles) of sodium in 1 l. of ethanol, maintained hot enough to prevent solidification, was added over 1.5 hr to *trans*-1,4-dichloro-2-butene[13] (125 g, 1.0 mole) with stirring and enough heat to maintain a gentle reflux. The mixture was refluxed for 2 hr after the addition was completed and then allowed to come to room temperature overnight.

The mixture was filtered, the alcohol was distilled, and the residue was treated with water. Ether extraction and drying were followed by distillation to give several very broad[14] fractions. Fraction 1 [forerun up to 135° (4 mm)] weighed 55 g; fraction 2 [135–177° (4 mm)] weighed 75 g; fraction 3 [180–260° (3 mm)] weighed 65 g. Only polymeric residue remained. Repeated distillation of the last two fractions gave 55 g of a light yellow liquid, bp 188–198° (10 mm), n^{24}_{D} 1.4520. Gas chromatographic purification[15] gave a colorless liquid, bp 190° (8 mm), n^{24}_{D} 1.4502.

Anal. Calcd for $C_{17}H_{30}O_5$: C, 64.94; H, 9.55. Found: C, 64.51; H, 9.52.

B.—A solution of 170 g (1.0 mole) of 2-carbethoxycyclohexanone in ethanolic sodium ethoxide prepared from 24 g (1.04 g-atoms) of sodium in 1 l. of ethanol was added to 1-chloro-4-ethoxy-2-butene as above. A similar work-up and distillation gave 88 g of forerun bp 163° (6 mm), 36.7 g of yellow liquid, bp 163–200° (7 mm), and 86 g of polymeric residue. The middle fraction gave a sample of colorless liquid, bp 185–90° (9 mm), n^{21}_{D} 1.4520, whose chromatographic retention time and infrared spectrum were identical with the product obtained by the reaction with 1,4-dichloro-2-butene.

Ethyl 5-Carbethoxy-9-ethoxy-7-nonenoate. **A.**—Except that the 1,4-dichloro-2-butene was added to the solution of 1 mole of 2-carbethoxycyclopentanone in the sodium ethoxide, the procedure was the same as the one used in the preparation of II. Distillation gave 93.5 g of forerun, 42.0 g of colorless liquid, bp 154–161° (1.0 mm), n^{25}_{D} 1.4484, and 79.1 g of residue, mostly polymeric.

Anal. Calcd for $C_{16}H_{28}O_5$: C, 64.00; H, 9.33. Found: C, 63.88; H, 9.35.

B.—In the same manner 134.5 g (1.0 mole) of 1-chloro-4-ethoxy-2-butene was added to a solution of 156 g (1.0 mole) of 2-carbethoxycyclopentanone in ethanolic sodium ethoxide prepared from 23 g (1.0 g-atom) of sodium and 1 l. of ethanol. Distillation gave 101.2 g of forerun, 31.9 g of colorless liquid, bp 161–174° (3.0 mm), n^{23}_{D} 1.4488, and 53.3 g of residue. The infrared spectra of this liquid and the one obtained from 1,4-dichloro-2-butene were identical.

2-Carbethoxy-2-(4-ethoxy-2-buten-1-yl)cyclohexanone (III).—Using 0.25 mole of each reactant and 250 ml of *t*-amyl alcohol, the sodium salt of 2-carbethoxycyclohexanone was added to 1-chloro-4-ethoxy-2-butene. The reaction yielded, in addition to 12 g of forerun and 20 g of polymeric residue, 16 g of light yellow liquid, bp 130–150° (1 mm), n^{25}_{D} 1.4738. The infrared

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[3] R. Cornubert and C. Borrel, *Bull Soc. Chim. France*, **47**, 305 (1930).

[4] W. B. Renfrow and G. B. Walker, *J. Am. Chem. Soc.*, **70**, 3957 (1948).

[5] W. B. Renfrow, *ibid.*, **66**, 144 (1944).

[6] C. R. Hausser and W. B. Renfrow, *ibid.*, **59**, 1823 (1937); **60**, 463 (1938).

[7] Refluxing with 20% *t*-amylate isomerized ethyl 1-carbethoxy-2-oxocyclohexaneacetate to ethyl 3-carbethoxy-2-oxocyclohexaneacetate by means of a ring cleavage followed by reclosure. Treatment with 4% *t*-amylate at room temperature, conditions much more like those prevailing after the initial formation of III, however, left the ethyl 1-carbethoxy-2-oxocylohexaneacetate unchanged.

[8] R. D. Sands, *J. Org. Chem.*, **28**, 1710 (1963).

[9] R. D. Sands, *ibid.*, **29**, 2488 (1964).

[10] Reported n^{20}_{D} 1.4437. U. S. Patent 2,462,830 (1949); *Chem. Abstr.*, **43**, P3968*g* (1949).

[11] F. Ramirez and J. W. Sargent, *J. Am. Chem. Soc.*, **77**, 6297 (1955).

[12] N. J. Leonard, H. S. Gutowsky, W. J. Middleton, and E. M. Peterson, *ibid.*, **74**, 4070 (1952).

[13] Either isomer could be used with the same result.

[14] The amount of polymerization, the amount of decomposition during distillation, and the amount of useful product varied considerably over several apparently identical runs.

[15] Using an Aerograph A-700 Autoprep with a 0.25 in. × 12 ft. column packed with 20% silicone stopcock grease on 60/80 mesh firebrick at a hydrogen flow of about 100 cc/min at a column temperature of 210°.

spectrum showed both carbonyl and ester absorption. By the absence of absorption between 1600 and 1700 cm^{-1} and by the failure to give a purple color with alcoholic ferric chloride, the carbethoxy and ethoxybutenyl groups were shown to be on the same carbon.[16] Gas chromatographic purification and a final distillation[15] gave a colorless liquid, bp 132–133° (1 mm), $n^{21}\mathrm{D}$ 1.4745.

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 8.95. Found: C, 67.32; H, 8.97.

2-Carbethoxy-2-(4-ethoxy-2-butene-1-yl)cycloheptanone. A.—Addition of *trans*-1,4-dichloro-2-butene (0.396 mole) to a solution of 2-carbethoxycycloheptanone (0.396 mole) in ethanolic sodium ethoxide prepared from 18.2 g (0.792 g-atom) of sodium in 400 ml of ethanol produced 41.4 g of liquid, bp 143–170° (1.5 mm), $n^{22}\mathrm{D}$ 1.4709. Redistillation gave a colorless liquid, bp 155° (1.5 mm), $n^{23}\mathrm{D}$ 1.4728.

Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.09; H, 9.23. Found: C, 68.40; H, 9.25.

B.—Addition of 1-chloro-4-ethoxy-2-butene to the sodium salt of 2-carbethoxycycloheptanone in 250 ml of ethyl alcohol, using 0.45 mole of each reactant, gave 37.0 g of liquid, bp 155–160° (2 mm), $n^{23}\mathrm{D}$ 1.4732. Gas chromatographic purification and a final distillation[15] gave a colorless liquid, bp 142° (1 mm), $n^{25}\mathrm{D}$ 1.4759. The infrared spectrum was identical with that of the product obtained by the 1,4-dichloro-2-butene reaction.

C.—Addition of 1-chloro-4-ethoxy-2-butene (0.0231 mole) to a solution of 2-carbethoxycycloheptanone (0.0231 mole) in 30 ml of *t*-amyl alcohol in which 0.51 g (0.0231 g-atom) of sodium had been dissolved produced 0.55 g of forerun, bp 140° (1 mm), 1.40 g of product, bp 145–160° (1 mm), $n^{22}\mathrm{D}$ 1.4769, whose infrared spectrum was identical with that of the fraction above with bp 142° (1 mm), and 2.2 g of residue.

2-Carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone.—Reaction of 78 g (0.5 mole) of 2-carbethoxycyclopentanone with 67.3 g (0.5 mole) of 1-chloro-4-ethoxy-2-butene in the presence of sodium *t*-amylate gave 15.7 g of forerun, 33.0 g of a yellowish liquid, bp 130–200° (1 mm), $n^{24}\mathrm{D}$ 1.4660, and 30 g of polymeric residue. Gas chromatographic purification[15] gave a colorless liquid, bp 123–125° (0.5 mm), $n^{22}\mathrm{D}$ 1.4695.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 66.20; H, 8.55.

Treatment of Ethyl 1-Carbethoxy-2-oxocyclohexaneacetate with Sodium *t*-Amylate. A.—A solution of 0.92 (0.04 g-atom) of sodium in 108 ml (1.0 mole) of *t*-amyl alcohol, a 4% solution,[11] was treated with 20 g of ethyl 1-carbethoxy-2-oxocyclohexaneacetate. After it had been stirred at room temperature for 24 hr, the mixture was acidified, taken up in ether, washed with water, and dried. Distillation gave 18 g of liquid, bp 145° (1 mm), and 2 g of polymeric residue. Redistillation gave 13.0 g of colorless liquid, bp 125–130° (1 mm), $n^{24}\mathrm{D}$ 1.4646, whose infrared spectrum was identical with that of the starting material.

B.—To a *t*-amylate solution prepared from 54 ml (0.5 mole) of *t*-amyl alcohol and 2.3 g (0.1 g-atom) of sodium, a 20% solution,[11] was added 22.6 g of ethyl 1-carbethoxy-2-oxocyclohexaneacetate. The mixture was refluxed for 8 hr and worked up as above. Distillation gave 11.0 g of crude material, bp 135–150° (1.5 mm), $n^{25}\mathrm{D}$ 1.4725. These properties, the infrared spectrum, and the coloration of alcoholic ferric chloride established the structure as ethyl 3-carbethoxy-2-oxocyclohexaneacetate.

α-(δ-Valeric acid)-γ-vinyl-γ-valerolactone (IV).—Ethyl 6-carbethoxy-10-ethoxy-8-decenoate (II), 42 g, was refluxed overnight with 300 ml of 10% hydrochloric acid. The mixture was then cooled and taken up in ether. The ether solution was washed with water and then with sodium bicarbonate solution. The sodium bicarbonate solution was washed with ether and then acidified to give 10.6 g of a white solid.[17] Recrystallization from toluene gave a pure white solid melting at 94°.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.23; H, 7.60. Found: C, 62.26; H, 7.71.

Spiro[4.5]dec-2-en-6-ene.—A solution of 46 g (2.0 g-atoms) of sodium in 1 l. of *t*-amyl alcohol was evaporated to dryness and 1500 ml of toluene was added to the residue. A mixture of 125 g (1.0 mole) of *cis*-1,4-dichloro-2-butene[18] and 98 g (1.0 mole) of cyclohexanone was kept at a gentle reflux for 48 hr. After cooling, 200 ml of water and 400 ml of 10% hydrochloric acid were added and the mixture was separated, dried, and distilled to give 27 g of fraction 1, bp 60–72° (3 mm), $n^{24}\mathrm{D}$ 1.4747; 20 g of fraction 2, bp 72–74° (3 mm), $n^{24}\mathrm{D}$ 1.4939; 14 g of fraction 3, bp 74–85° (3 mm), $n^{24}\mathrm{D}$ 1.4973; and 8 g of fraction 4, bp 100–110° (2 mm), $n^{24}\mathrm{D}$ 1.5067. Fraction 5 consisted of polymeric residue. The second and third fractions were combined and separated from cyclohexylidenecyclohexanone contaminant by gas chromatography[15] to give a colorless liquid, bp 73° (2 mm), $n^{25}\mathrm{D}$ 1.4951; 2,4-dinitrophenylhydrazone, mp 119–120°.

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.82; H, 9.42.

Spiro[4.5]decan-6-one.—A solution of 9 g of spiro[4.5]dec-2-en-6-one in 90 ml of 95% alcohol was treated with 1.0 g of palladium-on-barium sulfate catalyst (Englehard) and placed in the Parr low-pressure hydrogenator. After 8 hr of shaking at room temperature, 96% of the theoretical amount of hydrogen had been absorbed, and the mixture was filtered and concentrated to give 7.5 g of liquid. Gas chromatographic purification[15] gave a colorless liquid, $n^{21}\mathrm{D}$ 1.4870, whose 2,4-dinitrophenylhydrazone melted at 117–118° and showed no depression on mixture with the 2,4-dinitrophenylhydrazone of spiro[4.5]decan-6-one.[19]

Registry No.—II, 13958-65-1; III, 14002-05-2; IV, 13958-66-2; 1,4-dichloro-2-butene, 764-41-0; ethyl 5-carbethoxy-9-ethoxy-7-nonenoate, 13958-67-3; 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone, 13958-68-4; 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone, 13958-69-5; spiro[4.5]dec-2-en-6-one, 14054-26-3; 2,4-dinitrophenylhydrazone of spiro[4.5]dec-2-en-6-one, 13958-70-8.

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[16] The infrared spectra[12] and the ferric chloride test[11] were used to distinguish between ethyl 1-carbethoxy-2-oxocyclohexaneacetate and ethyl 3-carbethoxy-2-oxocyclohexaneacetate.

[17] When a sample of crude II was hydrolyzed, a crude IV and a bicarbonate-insoluble liquid, found to be III, were isolated. Heating the crude IV with quinoline gave a trace of Ic, thereby indicating the presence of Ib.

[18] When the *trans* isomer was used, the product was much more seriously contaminated with cyclohexylidenecyclohexanone.

[19] R. D. Sands and D. G. Botteron, *J. Org. Chem.*, **28**, 2690 (1963).

Reactions of Phenylmagnesium Bromide with Sterically Hindered Cyclobutanones. III. The Mechanism of Grignard Addition to These Carbonyl Groups[1,2]

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Received May 16, 1067

The results presented here indicate that, in the addition of a Grignard to the carbonyl groups studied, the Grignard species containing the group to be added to the carbonyl carbon is not coordinated to the carbonyl oxygen.[2]

Sterically hindered cyclobutanones, such as I[3,4] and II,[5] undergo three types of reaction with Grignard reagents.[6] A methylmagnesium halide adds to the carbonyl group of I normally to produce a tertiary

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[1] (a) Presented in part at the Meeting of the Georgia Academy of Sciences, Statesboro, Ga., April 22, 1966, Abstracts p 70; (b) research supported by the Petroleum Research Fund administered by the American Chemical Society, Grant-1867-B.

[2] Paper II. R. D. Kimbrough and R. D. Hancock, *Chem. Ind.* (London), 1180 (1965).

[3] H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920).

[4] E. Bergmann and O. Blum-Bergmann, *J. Chem. Soc.*, 727 (1938).

[5] C. D. Hurd and R. D. Kimbrough, *J. Am. Chem. Soc.*, **82**, 1373 (1960).

[6] R. D. Kimbrough, *J. Org. Chem.*, **28**, 3577 (1963).