which was dibrominated by using *N*-bromosuccinimide/benzoyl peroxide.[26] The dibromide was treated with KCN, and the resulting 6-amino-5-cyanodibenzocycloheptatriene was treated with concentrated sulfuric acid to give **1**, which was further purified by crystallization from ethanol;[27] mp 77 °C (lit.[27] mp 76–78). 2,2′-Dimethylbiphenyl was available from the first step of the above synthesis and was purified by distillation followed by chromatography. Biphenyl and xanthone were recrystallized before use, and 1,3-cyclohexadiene was distilled. Aberchrome-540 was used as received from Aberchromics Ltd., Cardiff, U.K. Solvents were Aldrich gold label or spectrograde and were used as received.

General. Fluorescence and phosphorescence spectra were measured on a Perkin-Elmer LS-5 spectrofluorimeter. GC analyses were done on a Perkin-Elmer 8320 instrument equipped with a 12-m BP1 capillary column. GC/MS spectra were recorded on a Hewlett-Packard 5995 instrument equipped with a 10-m Ultra I (OV-101) capillary column.

Laser Flash Photolysis. The basic laser flash photolysis equipment as well as the modifications required for two-laser experiments has been described.[28,29] A Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm, 5-ns pulses, ≤20 mJ/pulse), a Molectron UV-24 nitrogen laser (337 nm, ~8-ns

pulses, ≤15 mJ/pulse), and a Candela flash pumped dye laser (Stilbene 420 dye in 50% aqueous methanol; 100–200 mJ/pulse; ~250-ns pulses) were used for sample excitation. Samples were contained in 7 × 7 mm^2 quartz cells and were deaerated by nitrogen purging.

Preparative Photolysis of 1. A solution of 100 mg of **1** in 50 mL of benzene was deaerated and then irradiated for 80 h by using RPR-3000 lamps. GC analysis showed 85% conversion to a single product in >90% yield. The product was separated by low-pressure chromatography on silica gel using hexane as eluent. It was confirmed to be dihydrophenanthrene by comparison of its GC/MS and NMR spectra with those of an authentic material.

Quantum Yields. Quantum yields for the disappearance of **1** in benzene were measured by using the formation of acetophenone from valerophenone in benzene as an actinometer (Φ = 0.30).[14] Samples of **1** and valerophenone with matched optical densities at 310 nm were deaerated and irradiated with RPR-3000 lamps to ~10% conversion. Quantitative analyses were done by GC using appropriate internal standards and calibration solutions.

Two-Laser Photolyses. Three separate aliquots of a 1.1 mM benzene solution of **1** were irradiated with (a) 500 308-nm pulses, (b) 500 pairs of 308-nm plus 430-nm pulses with a 0.5-μs delay between the two lasers, and (c) 500 pairs of pulses with the reverse sequence of b. Product analysis by GC against an internal standard showed 2.5, 8.0, and 2.6% dihydrophenanthrene for a, b, and c, respectively.

Acknowledgment. We thank S. E. Sugamori for technical assistance and Dr. J. C. Scaiano for helpful discussions.

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Alkylenation with Geminal Dialuminoalkane Reagents: The Synthesis of Olefins from Ketones[1]

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Bis(dichloroalumino)methane (BDAM, **1**) has been synthesized in high yield from aluminum powder and methylene chloride by a published procedure carefully modified for safety. By the screening away of aluminum metal fine particles and the gradual addition of methylene bromide promoter over the course of reaction, a safe procedure was attained. Although **1** itself was a poor methylenating agent for ketones, its dietherate complex was distinctly more reactive. By exchanging half the halogens of **1** with Me$_3$Al, MeMgBr, or Et$_3$Al, two very effective methylenating agents for ketones, namely CH$_2$(AlClMe)$_2$ (**2**) and CH$_2$(AlClEt)$_2$ (**3**), were obtained. As dietherates with Et$_2$O or THF, **2** and **3** smoothly converted a broad variety of ketones (aliphatic, alicyclic, and aromatic) into their corresponding methylene derivatives, with little or no competitive alkylation or reduction. A titanium-modified reagent, Cl$_2$AlCH$_2$TiCl$_3$ (**4**), was also effective toward ketones, but gave only low conversions of esters to vinyl ethers. Finally, as an example of a multicarbon, alkylenating agent, the reagents **5–7** ((R$_2$Al)$_2$CH(CH$_2$)$_4$CH$_3$, **5**, R = Et; **6**, R = Cl; and **7**, R = Cl or Et) were examined. Good to fair yields of alkylenation were obtained with aromatic ketones, but aliphatic ketones underwent alkylation, hydride reduction, and/or aldol condensation. The great influence of alkyl groups and donor solvent on the reactivity of **1–3** is briefly discussed.

The alkylenation of carbonyl compounds, the so-called carbonyl olefination reaction (eq 1),[2] became a feasible transformation with the discovery of the methylenating action of methylenetriphenylphosphorane by Wittig and Geissler in 1953 (eq 1, A = Ph$_3$P).[3] In the succeeding 35 years such Wittig reactions have been widely applied in
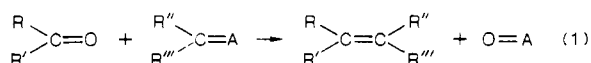
organic synthesis, in general,[4,5] and in natural product or pharmaceutical synthesis, in particular.[6] Although the Wittig reaction is general for aldehydes and ketones and

$$\underset{R'}{\overset{R}{>}}C=O \; + \; \underset{R'''}{\overset{R''}{>}}C=A \; \longrightarrow \; \underset{R'}{\overset{R}{>}}C=C\underset{R'''}{\overset{R''}{<}} \; + \; O=A \quad (1)$$

(1) Part 43 of the series Organometallic Compounds of Group III. Part 42: *Proceedings of the Symposium on Transition Metal Catalyzed Polymerization (1986): The Ziegler-Natta and Methathesis Polymerizations*; Quirk, R. P., Ed.; Cambridge University: New York, 1988.
(2) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum: New York, 1983; p 69.
(3) Wittig, G.; Geissler, G. *Justus Liebigs Ann. Chem.* **1953,** *580,* 44.
(4) Maercker, A. In *Organic Reactions*; Cope, A. C., Ed.; John Wiley: New York, 1965; Vol. 14, p 270.
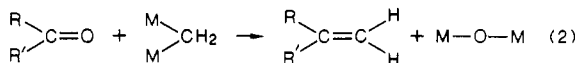(5) Johnson, A. W. *Ylid Chemistry*; Academic: New York, 1966.
(6) Reference 4, p 354–377.

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‡State University of New York at Binghamton.

the phosphorane reagent adaptable to allow R'' and R''' to be non-hydrocarbon substituents, the phosphorane reagents and the lithium alkyls often used to generate them are expensive and also very basic. The latter property can be the cause of undesired side reactions, such as enolization and aldol condensation.[7]
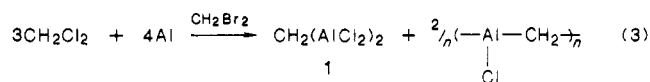
In the search for less expensive, readily accessible alkylenating agents, we have considered employing the geminal dimetallomethanes of lithium,[8] magnesium,[9] and aluminum.[10] The transformation depicted in eq 2 has been reported to proceed with the corresponding dilithio-,[11,12] dizincio-,[13] and bis(halomagnesio)methanes,[9] but

$$R_2C=O + \begin{matrix} M \\ M \end{matrix}CH_2 \longrightarrow \begin{matrix} R \\ R' \end{matrix}C=C\begin{matrix} H \\ H \end{matrix} + M-O-M \quad (2)$$

bis(dibromoalumino)methane is reported to be rather unreactive toward ketones.[10] Since the lithium,[8] zinc,[13] and magnesium reagents[14,15] are either expensive or difficult to make, we have examined the cheaper aluminum analogues, in the hope that their reactivity toward ketones might be raised by using different ligands on aluminum or changing the reaction solvent. Indeed, just such variations have led us to uncover geminal dialuminomethanes that methylenate a broad range of ketones. To a more limited extent, 1,1-dialuminoalkanes have also been found to alkylenate aromatic ketones.

Results

Synthesis of Organoaluminum Methylenating Agents.
By careful modification of various published descriptions,[16-18] a safe procedure for preparing bis(dichloroalumino)methane (BDAM, 1) on a 0.33 molar scale from methylene chloride and aluminum power was developed (eq 3). Direct mixing of all the CH_2Br_2 initiator

$$3CH_2Cl_2 + 4Al \xrightarrow{CH_2Br_2} CH_2(AlCl_2)_2 + \tfrac{2}{n}(-Al-CH_2\tfrac{}{n} \quad (3)$$
$$\underset{1}{} \qquad \underset{Cl}{}$$

to the unscreened aluminum powder can lead to explosive mixtures,[19] but the careful removal of fine particles of aluminum and the gradual addition of CH_2Br_2 once the reaction has started led to the smooth formation of BDAM (1). The solid BDAM could be suspended in toluene and treated with 2 molar equiv of THF to form soluble 1·2THF.

Bis(chloromethylalumino)methane (2) could be readily prepared by redistribution reactions of 1 with either tri-

methylaluminum (eq 4) or methylmagnesium bromide (eq 5). Since both reactions employed diethyl ether, reagent 2 was generated as the dietherate.
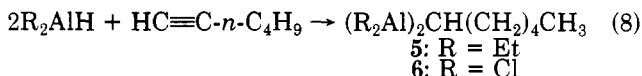
$$2MeMgBr \xrightarrow[eq\ 5]{} \underset{2}{CH_2(AlClMe)_2} \xleftarrow[eq\ 4]{} Me_3Al \quad (4, 5)$$
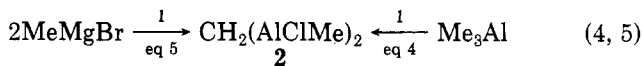
Bis(chloroethylalumino)methane (3) was generated from 1 and triethylaluminum in the presence of 2 molar equiv of diethyl ether or tetrahydrofuran (eq 6).

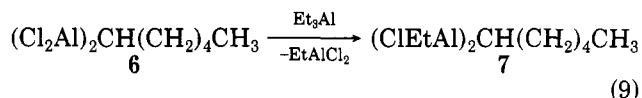$$\underset{1}{CH_2(AlCl_2)_2} + Et_3Al \xrightarrow[-EtAlCl_2]{CH_2Cl_2} \underset{3}{CH_2(AlClEt)_2} \quad (6)$$
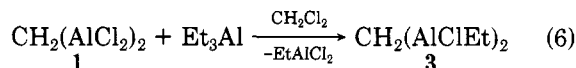
Finally, (dichloroalumino)(trichlorotitanio)methane (4) was made in situ by a 1:1 molar interaction between 1 and titanium(IV) chloride in THF (eq 7).

$$\underset{1}{CH_2(AlCl_2)_2} + TiCl_4 \xrightarrow[-AlCl_3]{THF} \underset{4}{Cl_2AlCH_2TiCl_3} \quad (7)$$
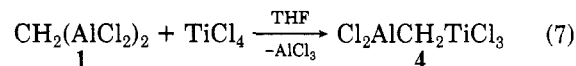
Syntheses of Organoaluminum Hexylenating Agents.
1,1-Bis(diethylalumino)hexane (5) and 1,1-bis(dichloroalumino)hexane (6) were made individually by adding 2 molar equiv of either diethylaluminum hydride (R = Et, eq 8) or dichloroaluminum hydride diethyl eth-

$$2R_2AlH + HC{\equiv}C\text{-}n\text{-}C_4H_9 \rightarrow (R_2Al)_2CH(CH_2)_4CH_3 \quad (8)$$
$$\underset{\substack{5:\ R = Et \\ 6:\ R = Cl}}{}$$

erate (R = Cl) to hexyne.[20-22] Alanogous to the preparation of 2 and 3, 1,1-bis(chloroethylalumino)hexane (7) was prepared from 6 by redistribution with Et_3Al (eq 9).

$$\underset{6}{(Cl_2Al)_2CH(CH_2)_4CH_3} \xrightarrow[-EtAlCl_2]{Et_3Al} \underset{7}{(ClEtAl)_2CH(CH_2)_4CH_3}$$
$$(9)$$

Methylenation of Ketones with Dialuminomethane Reagents.
Of the three types of dialuminomethanes, $CH_2(AlCl_2)_2$ (1), $CH_2(AlClR)_2$ (R = Me or Et) (2 or 3), and $CH_2(AlR_2)_2$, only the first two types were examined in the present study. The third type, as exemplified by CH_2-$(AlEt_2)_2$, had already been studied and had been shown to give methylenation and also ethylation and reduction products in competitive amounts (eq 10).[23]
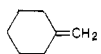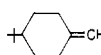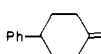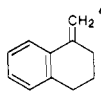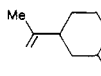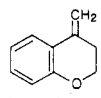

$$(10)$$
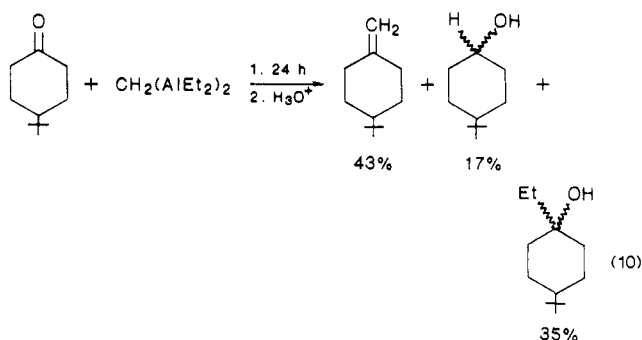
We were able to confirm the literature report that bis(dihaloalumino)methanes, as such, do not give satisfactory yields of methylene derivatives from ketones.[10] Thus, heating 1 with benzophenone[8] in refluxing toluene for 6 h gave only 30% of 1,1-diphenylethylene (9). But it is noteworthy that 1 as its bis complex with THF converted

(7) Wittig, G.; Böll, W.; Krück, K.-H. Chem. Ber. 1963, 95, 2514.

(8) West, R.; Rochow, E. G. J. Org. Chem. 1953, 18, 1739.

(9) Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. Tetrahedron 1970, 26, 1281.

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(16) Lehmkuhl, H.; Schäfer, R. Tetrahedron Lett. 1966, 2315.

(17) Mottus, E. H.; Ort, M. R. J. Electrochem. Soc. 1970, 117, 885.

(18) Ort, M. R.; Mottus, E. H. J. Organomet. Chem. 1973, 50, 47.

(19) In general, as many workers in this field have learned, the reaction of haloalkanes with aluminum metal can occur in a violent manner if the reaction is not properly initiated before too great a proportion of the reactants have been mixed: cf. Grosse, A. V.; Mavity, J. J. Org. Chem. 1940, 5, 106 and Thomas, W. H. Ind. Eng. Chem., Prod. Res. Dev. 1982, 21, 120-122.
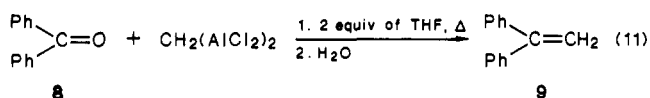
(20) Wilke, G.; Müller, H. Justus Liebigs Ann. Chem. 1960, 629, 222.

(21) Zweifel, G.; Steele, R. B. Tetrahedron Lett. 1966, 6021.

(22) Eisch, J. J.; Gopal, H.; Rhee, S. G. J. Org. Chem. 1975, 40, 2064.

(23) Ashby, E. C.; Smith, R. S. J. Organomet. Chem. 1982, 225, 71.

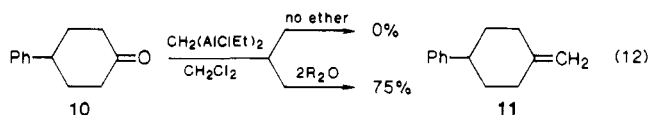**Table I. Reactions of Dialuminomethane Reagents with Ketones**

ketone	$CH_2(AlR_2)_2 \cdot 2D$	solvent	time, h	temp, °C	product[b]	% yield[a]
benzophenone (8)	R = Cl; D = none	PhMe	6	110	$Ph_2C{=}CH_2$ (9)	30
benzophenone (8)	R = Cl; D = THF	PhMe	16	110	9	82
benzophenone (8)	R = Cl, Et; D = THF	PhMe	48	25	9	70
cyclohexanone (12)	R = Cl; D = THF	CH_2Cl_2	17	25	(cyclohexane=CH_2)	50
4-*tert*-butylcyclohexanone (13)	R = Cl, Et; D = THF	CH_2Cl_2/C_6H_{14}	17	25	(4-tert-butylmethylenecyclohexane)[c]	70
4-phenylcyclohexanone (10)	R = Cl, Et; D = Et_2O	CH_2Cl_2	3	25	Ph–(cyclohexane)=CH_2 (11)[d]	75
4-phenylcyclohexanone (10)	R = Cl, Me; D = Et_2O	CH_2Cl_2	3	25	11	89
α-tetralone (14)	R = Cl, Me; D = Et_2O	PhMe	0.5, 3	100, 25	(1-methylene-tetralin)[e]	66
dihydrocarvone (15)	R = Cl, Me; D = Et_2O	CH_2Cl_2	3	25	(isopropenyl-methylenecyclohexane)[f]	95
4-chromanone (16)	R = Cl, Me; D = Et_2O	CH_2Cl_2	0.5	25	(4-methylenechromane)[g]	61
diisopropyl ketone (17)	R = Cl, Me; D = Et_2O	CH_2Cl_2	30	25	$(Me_2CH)_2C{=}CH_2$	79

[a] Isolated yield. [b] Except where unreported compounds were formed, the products were identified with IR, MS, and ^{1}H NMR data and comparison with known samples. [c] Carlson, R. G.; Behn, N. S. *J. Organomet. Chem.* **1967**, *32*, 1363. [d] IR (neat) 1650 and 885 cm^{-1} (C=CH_2); ^{1}H NMR (CDCl$_3$) δ 1.20–2.87 (m, 9 H), 4.54 (s, 2 H), and 7.18 (s, 5 H); MS, *m/e* 172 (P). Anal. Calcd for C$_{13}$H$_{16}$: C, 90.63; H, 9.36. Found: C, 90.55; H, 9.47. [e] Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, G.; Gallego, H.; Tijerina, T.; Pine, R. D. *J. Organomet. Chem.* **1985**, *50*, 1212. [f] IR (neat) 1645 and 885 cm^{-1} (C=CH_2); ^{1}H NMR (CDCl$_3$) δ 1.1 (m, 5 H), 1.50–2.29 (m, 9 H), and 4.63 (m, 4 H). Anal. Calcd for C$_{10}$H$_{18}$: C, 86.88; H, 13.12. Found: C, 86.97; H, 12.85. [g] Narula, L. K.; Mark, K. T.; Kao, L.; Xu, Y.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 3899.
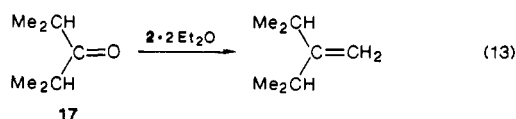
8 into 9 in an 82% yield (eq 11). Equally satisfactory with this ketone was 3, $CH_2(AlClEt)_2$ as its THF solvate, which after 48 h at 25 °C gave a 70% yield of 9.

$$Ph_2C{=}O + CH_2(AlCl_2)_2 \xrightarrow[\text{2. H}_2\text{O}]{\text{1. 2 equiv of THF, }\Delta} Ph_2C{=}CH_2 \quad (11)$$

$$\mathbf{8} \qquad\qquad\qquad \mathbf{9}$$

In fact, with enolizable ketones it was essential to employ 2 and 3 as their dietherates (Et$_2$O or THF), if any methylenation at all was to be obtained. The behavior of 4-phenylcyclohexanone (10) provides a dramatic comparison (eq 12). In the absence of ethers, 3 tends to promote aldol condensations of the substrate ketones.
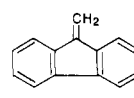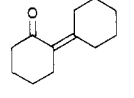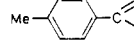
$$Ph{-}(\text{cyclohexanone}){=}O \xrightarrow[\text{CH}_2\text{Cl}_2]{CH_2(AlClEt)_2} \begin{cases} \xrightarrow{\text{no ether}} 0\% \\ \xrightarrow{2R_2O} 75\% \end{cases} Ph{-}(\text{cyclohexane}){=}CH_2 \quad (12)$$

$$\mathbf{10} \qquad\qquad\qquad\qquad \mathbf{11}$$

A wide variety of other ketones, such as cyclohexanone (12), 4-*tert*-butylcyclohexanone (13), α-tetralone (14), dihydrocarvone (4-(2-isopropenyl)-2-methylcyclohexanone) (15), and 4-chromanone (16), gave yields of isolated methylenation products in the range of 50–90%. Even the sterically hindered diisopropyl ketone (17) underwent smooth methylenation (eq 13). The results are gathered for comparison in Table I.

$$\underset{\text{17}}{\underset{Me_2CH}{\overset{Me_2CH}{>}}C{=}O} \xrightarrow{\mathbf{3 \cdot 2Et_2O}} \underset{Me_2CH}{\overset{Me_2CH}{>}}C{=}CH_2 \quad (13)$$
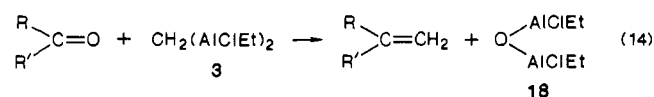
The minor reaction products in these methylenations with the etherate of 3 were not alkylated products but rather alcohols resulting from reduction. Such reductions (5–15%) were not due to 3 itself, but stemmed from the

Table II. Reactions of $Cl_2AlCH_2TiCl_3$ with Carbonyl Substrates

carbonyl substrate	solvent	time, h	temp, °C	product	% yield[a]
benzophenone (8)	PhMe	0.5	110	$Ph_2C{=}CH_2$ (9)	100
9-fluorenone	PhMe	0.25	110	(9-methylenefluorene)	82
cyclohexanone (12)	PhMe	3.0	25	(cyclohexylidenecyclohexanone)	60
methyl p-methyl-benzoate	PhMe	72	25	$Me{-}C_6H_4{-}C({=}CH_2)OMe$	30[b]

[a] Isolated yield. [b] Yield estimated by ^{1}H NMR spectral analysis of the isolated organic fraction.

dialuminoxane byproduct 18, which is a most powerful reducing agent (eq 14).[24]

$$\underset{R'}{\overset{R}{>}}C{=}O + CH_2(AlClEt)_2 \longrightarrow \underset{R'}{\overset{R}{>}}C{=}CH_2 + O{<}\underset{AlClEt}{\overset{AlClEt}{}} \quad (14)$$

$$\qquad\qquad \mathbf{3} \qquad\qquad\qquad\qquad\qquad \mathbf{18}$$

Methylenation with (Dichloroalumino)(trichlorotitanio)methane (4). By use of this titanium-modified aluminomethane, it was hoped that enhanced activity toward ketones would result in higher yields of olefins. Furthermore, as with the Tebbe reagent, Cp$_2$TiCH$_2$·Me$_2$AlCl,[25] it was expected that 4 might also be able to convert esters to vinyl ethers.[26] As is evident from Table

(24) Eisch, J. J.; Boleslawski, M. P., unpublished studies, 1986.
(25) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043.

II, these aims were partly realized, for **4** converted benzophenone and fluorenone into their methylene derivatives in high yield. On the other hand, **4** proved to be much more acidic and thus cyclohexanone largely underwent an aldol condensation. However, **4** converted only about a third of methyl *p*-methylbenzoate (**19**) into its vinyl ether (**20**), even when the workup was performed in the presence of Et$_3$N to scavenge the great amount of HCl set free on hydrolysis (eq 15). In an attempt to lower the Lewis

$$(15)$$
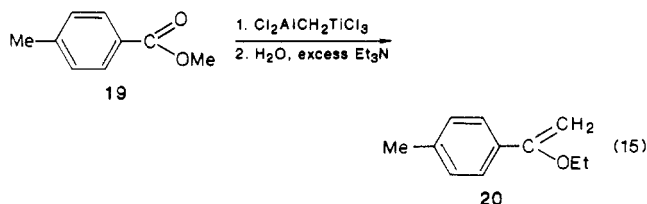
acidity of the methylenating agent and to reduce the amount of HCl set free on hydrolysis, titanium(IV) isopropoxide was substituted for TiCl$_4$. Unfortunately, a much inferior methylenating agent resulted.

Hexylenation of Ketones with Organoaluminum Agents. As a test substrate, benzophenone was allowed to react with 1,1-dialuminohexanes **5–7**. Reagents **6** and **7** gave fair to good conversion to 1,1–diphenyl-1-heptene (eq 16). But reagents with ethyl groups gave significant

$$(16)$$

9% (**5**: R = Et)
71% (**6**: R = Cl)
55% (**7**: R = Cl, Et)
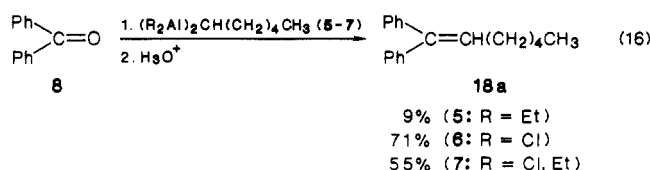
amounts of reduction and ethylation products (**5**, 95%; **7**, 28%). Even reagent **6** gave 29% reduction of **8**, but the hexylenation product **18a** could be readily isolated by distillation. With aliphatic aromatic ketones, like acetophenone (**19a**), reagent **6** yielded a mixture of reduction (15%), hexylenation (**20a**, 51%), and aldol condensation (**21**, 34%) (eq 17).

$$(17)$$
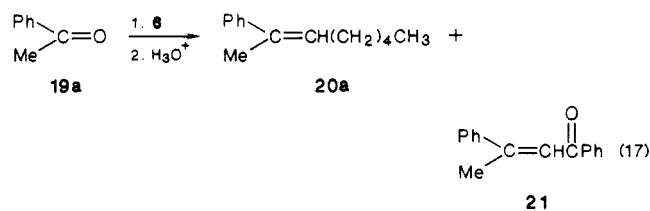
Wholly aliphatic ketones proved to be completely unsatisfactory in the hexylenation reaction. For example, cyclohexanone (**12**) was converted by **6** into a 76:34 mixture of cyclohexanol (**22**) and 2-cyclohexylidenecyclohexane (**23**) (eq 18). With reagent **7**, cylcohexanone was almost completely ethylated (95%) and aldol condensation was minor.

$$(18)$$
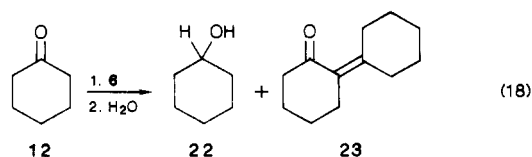
Discussion

The most striking feature of geminal dialuminoalkanes is the heightened reactivity of their carbon–aluminum

(26) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

Scheme I
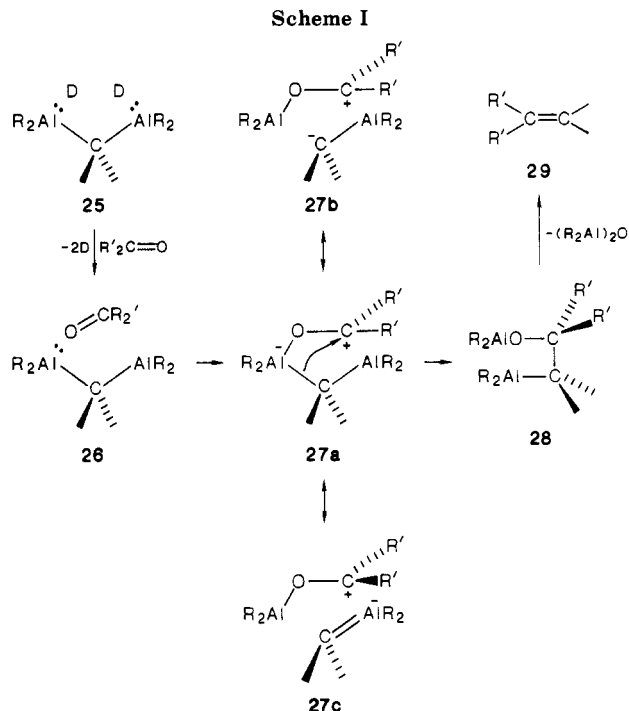
bonds, in comparison with that of simple aluminum alkyls (cf. also eq 10[23]). The dialuminomethanes, **2** and **3** (CH$_2$(AlClR)$_2$ (where R = Me or Et), have an equal number of CH$_2$–Al and R–Al bonds, but it is the CH$_2$–Al bond that preferentially reacts with the ketonic substrates studied here. Little or no sign of methylated or ethylated products from ketones was detected. Even with 1,1-dialuminohexanes **5** and **7**, (R$_2$Al)$_2$CH(CH$_2$)$_4$CH$_3$ (where one or both R = Et), their response to aromatic ketones was also mostly at the hexylidene carbon–aluminum bonds. Only with aliphatic ketones, like cyclohexanone, did the amount of ethylation by **7** become the predominant reaction. In this case and in that of other aliphatic ketones, it is likely that the greater steric demand of the hexylidene group is the reason for preferential insertion of the ketone at the ethyl–aluminum bond (**24**). Such steric hindrance
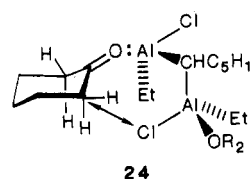
should not be so severe with aromatic ketones, so the inherently greater reactivity of the AlCH–Al bond can determine the site of reaction (eq 16).

The electronic origin of geminal dialuminum–carbon bond reactivity can be understood in terms of a greater tendency for its heterolysis in the transition state of ketone insertion (Scheme I). The basic properties of a ketone permits the dialuminoalkane dietherate **25** to form complex **26**.[27] The heterolysis of the carbon–aluminum bond (**27a**) is facilitated by the delocalization of the R$_2$AlC$^-$ carbanion (**27b**) into the 3p$_z$ orbital of the adjacent aluminum (**27c**). The formation of **28** sets the stage for the highly exothermic loss of dialuminoxane, (R$_2$Al)$_2$O, just as in the imination of ketones by bis(dichloroaluminum) phenylimide.[28]

(27) Eisch, J. J.; Fichter, K. C. *J. Am. Chem. Soc.* **1975**, *97*, 4772.

Table III. Yields and Analyses of Bis(dichloroalumino)methane (1)

expt	Al, g[a]	CH$_2$Cl$_2$, mL	CH$_2$Br$_2$, mL	R$_3$Al, mL	% yield[b]	% Al[c]	% Cl[d]
1	14	200	14	Et, 2.0	88	23.1	55.4
2	20	260	16	Et, 3.0	85	22.2	54.9
3	14	250	12	Me, 1.0	83[e]	24.1	61.8
4	14	200	14	Me, 1.5	86	22.1	56.7

[a] Aluminum powder carefully sieved for particle size selection before reaction. [b] Yield : grams of product (wt % Al)/gram of Al used + gram in R$_3$Al used. [c] Aluminum analyses according to: Crompton, T. R. *Analysis of Organoaluminum and Organozinc Compounds*; Pergamon: London, 1968; p 27. [d] Chlorine analyses according to: Martin, A. *J. Anal. Chem.* **1958**, *30*, 233. [e] Product washesd with 200 mL of fresh CH$_2$Cl$_2$.

The superiority of ether complexes of reagents 1–7 appears, in general, to be due to a reduction of their Lewis acidity. Since dialuminoxanes, R$_2$Al–O–AlR$_2$, are themselves strong bidentate Lewis acids,[29] it is likely that unsolvated geminal dialuminoalkanes would exhibit a similar heightened acidity. Such acidity is undoubtedly responsible for enolate salt formation (30) and thereby for the aldol condensation observed to occur with reagents 1–7 (eq 19).

30
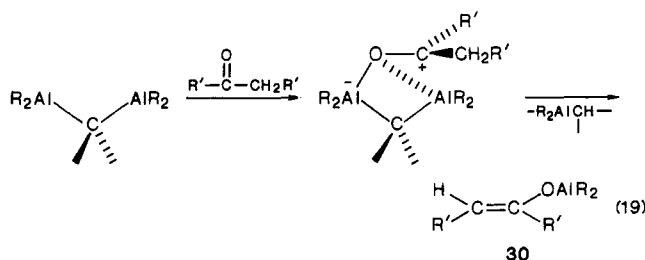
Experimental Section

General Procedures. All preparations and reactions involving these air- and moisture-sensitive organoaluminum reagents were conducted under an atmosphere of anhydrous, oxygen-free nitrogen in accordance with well-precedented published procedures.[30]

The reactions of the aluminum methylenating agents with the various carbonyl substrates, which are summarized in Table I, were worked up in the following manner (method A). After the carbonyl substrate had been added slowly to the methylenating agent at 20–25 °C and the reaction allowed to run to completion under the conditions indicated, the reaction mixture was poured cautiously into a slurry of ice and diethyl ether. The thawed mixture was acidified to aid the separation of distinct layers. The separated organic layer was washed with aqueous Na$_2$CO$_3$ and dried over anhydrous MgSO$_4$ and thereupon evaporated under reduced pressure to yield the crude product. Column chromatography on silica gel (Merck, grade 60, 230–900 mesh), first with hexane and then with hexane–CH$_2$Cl$_2$ (1:9 v/v) eluents generally gave analytically pure product (cf. procedure for 4-chromanone given below).

The reactions of the titanium-containing aluminum methylenating agents (method B) were worked up in this modified manner (Table II). After the methylenating agent and ketone had been allowed to react, the reaction mixture was hydrolyzed

with a minimum of water in the presence of Et$_3$N and suspended Ca(OH)$_2$, both of which acted as acid scavengers. The resulting hydrolyzed suspension was filtered and the filter cake washed with ether. The combined organic filtrate was concentrated to a small volume and the latter allowed to percolate through a short column of alumina, which had been made basic by pretreatment with Et$_3$N. Further chromatography was undertaken to isolate pure product (cf. preceding paragraph).

Starting Materials. Solvents. Toluene (technical grade) was dried over sodium metal, distilled under nitrogen, and stored over molecular sieves. The solvents, tetrahydrofuran (THF), diethyl ether, and methylene chloride (Aldrich, anhydrous grade, packed under nitrogen), were used as received. The ketonic substrates, benzophenone, cyclohexanone, methyl p-methylbenzoate, 4-tert-butylcyclohexanone, 4-phenylcyclohexanone, and dihydrocarvone, were commercially available in purities of 95% or better (Aldrich) and were also used as received. But the commercial products, 2,4-dimethyl-3-pentanone, α-tetralone, and 4-chromanone, were purified by fractional distillation. Methylene bromide was distilled and stored over molecular sieves.[31]

The aluminum powder was obtained from the Aluminum Corporation of America in 99.7% purity and ball-milled to 120 mesh.

Analytical Procedures. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrometer, Model 457, equipped with NaCl optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with a Varian spectrometer, Model EM-360, on 20% solutions of CDCl$_3$ or perdeuteriotoluene. The values are reported on the δ scale in parts per million with reference to internal tetramethylsilane, followed by the relative proton intensities and the coupling constants (*J*) in hertz. Mass spectra (MS) were measured with a Hewlett-Packard instrument, Model 5992, and are reported as to principal peaks (m/e) with relative intensities given in parentheses.

Quantitative analyses for aluminum and chlorine were conducted by the Texas Alkyls analytical section by conventional, published methods (Table III).

Preparation of Organometallic Reagents. Bis(dichloroalumino)methane (1, BDAM). *Caution:* The reaction between aluminum powder and methylene chloride can occur explosively,[19] if the aluminum powder used contains highly active fines and if the methylene bromide used as the initiator is added all at once at the beginning of the reaction. If sieving of the aluminum to remove such fines is performed and if the methylene bromide initiator is added gradually over a period of several hours, the preparation of BDAM can be performed safely and has been carried out repeatedly without incident.

The requisite aluminum powder was prepared in the following manner. A batch of aluminum powder (Alcoa, 120 mesh) was sieved and the powder of 90–150 mesh was collected. A 50-g batch was ball-milled as a suspension in Isopar-H,[32] which contained 2 mL of triethylaluminum. The resulting aluminum flakes were filtered off under nitrogen, washed with anhydrous pentanes, and dried in a stream of nitrogen. By resieving of this aluminum, the fraction of 12–35 mesh was isolated and then used for the preparation of BDAM.

Into a 300-mL, three-necked flask, which was dried and maintained under nitrogen and was equipped with a reflux condenser surmounted by a nitrogen inlet, a magnetic stirrer, and

(28) Eisch, J. J.; Sanchez, R. *J. Org. Chem.* **1986**, *51*, 1848. As a reasonable alternative to the formation of **29** from **28** by the elimination of (R$_2$Al)$_2$O, a referee has suggested that **28** may be the principal product of the reaction and that upon workup it undergoes hydrolysis to the corresponding alcohol and that the alcohol is subsequently dehydrated. We believe that this interpretation can be ruled out upon two grounds: (1) despite mild conditions of hydrolysis, no alcohol but only the olefin is ever detected; and (2) were an alcohol involved as an intermediate, its dehydration would not lead to the terminal or exocyclic C=CH$_2$ linkage but rather, as in the case of 12, 14, or 16, the endocyclic olefin product. Accordingly, even though the aluminoxane eliminated in these reactions has not been detected, we favor olefin formation through the step **28** → **29** rather than dehydration through an intermediate alcohol.

(29) Kunicki, A.; Serwatowski, J.; Pasynkiewicz, S.; Boleslawski, M. *J. Organomet. Chem.* **1977**, *128*, 21.

(30) Eisch, J. J. *Organometallic Syntheses*; Academic: New York, 1981; Vol. 2, pp 3–52.

(31) Reference 30, p 26.

(32) Isopar-H is a proprietary isoparaffinic hydrocarbon available from the Exxon Corp.

a thermocouple sensor, were placed 19.0 g (0.70 g-atom) of the prepared aluminum powder, 200 mL of dry methylene chloride, and 2 mL of triethylaluminum. After this mixture had been stirred for 15 min in an oil bath held at 52 °C, 2.0 mL of methylene bromide was introduced. (*Caution*: After the initial 2 mL charge of CH_2Br_2, additional CH_2Br_2 should be added only after the reaction has clearly been initiated. In any case, the initial charge of CH_2Br_2 should not exceed 20% of the total CH_2Br_2 used.) After 30 min of stirring under mild reflux, the aluminum particles darkened and more vigorous reflux commenced. Periodically over 30 min, six more 2-mL portions of CH_2Br_2 were introduced. At this point, almost all the aluminum had reacted and only a small amount of fine black powder remained. With maintenance of the nitrogen atmosphere, the reaction mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. The resulting BDAM, 55 g, was isolated as a tan solid. Analytical data for various typical runs are presented in Table III.

Bis(chloroethylalumino)methane (3). This reagent was prepared from BDAM, in situ, before each reaction with a carbonyl substrate. The BDAM was suspended in dry methylene chloride (5 g of BDAM/80 mL of CH_2Cl_2) at 10 °C and then treated with 2 molar equiv of diethyl ether (4 mL). After 30 min of stirring at 20–25 °C, a homogeneous solution was attained. Then the solution was recooled to 0 °C and 1 molar equiv of triethylaluminum was added.

Bis(chloromethylalumino)methane (2). This reagent was generated in situ, either by a redistribution with trimethylaluminum, similar to that described above for **3** or by reaction of BDAM with methylmagnesium bromide, as described here. Thus, BDAM (5.2 g, 25 mmol) was suspended in 80 mL of CH_2Cl_2 at 10 °C and 4 mL of diethyl ether introduced. When a solution was attained at 20–25 °C, it was recooled to 10 °C and treated with 13.2 mL of 3 M methylmagnesium bromide in diethyl ether over 30 min. After 1 h of stirring at 20–25 °C, the precipitated solids were removed by filtration under nitrogen and then washed with three 100-mL portions of CH_2Cl_2. The solvent was evaporated to 53 g of solution, which contained 2.36% of aluminum and 3.6% of chlorine.

(Dichloroalumino)(trichlorotitanio)methane (4). BDAM (50 mmol) was slowly treated with 100 mL of anhydrous THF at 0 °C, because the complexation is very exothermic. Then titanium tetrachloride (50 mmol in 200 mL of THF, whose dissolution should also be done at low temperatures) was added gradually at room temperature. The reaction mixture was thereupon warmed up to 55 °C for 10 min and then recooled to 25 °C where the THF was evaporated under reduced pressure. The resulting, semisolid red residue was dissolved in toluene to a final volume of 250 mL.

1,1-Dialuminohexanes (5–7). 1,1-Bis(diethylalumino)hexane (5) was prepared by modification of a published procedure.[33] In anhydrous toluene at 0 °C, pure 1-hexyne was treated with 1 molar equiv of diethylaluminum hydride (Texas Alkyls, 98%). Then at room temperature a second equivalent of hydride was added and the reaction solution heated to 90 °C for 4 h. The cooled solution was analyzed by hydrolysis of an aliquot: the collected C_6 hydrocarbon fraction was >98% composed of *n*-hexane.

1,1-Bis(dichloroalumino)hexane (6) was prepared from 1-hexyne and 2 molar equiv of dichloroaluminum hydride.[34] Thus, a suspension of 3.84 g (29 mmol) of aluminum chloride in 20 mL of pentane and 50 mL of anhydrous diethyl ether was rapidly treated with 9.6 mL of 1.0 M solution of lithium aluminum hydride in ether. After 60 min the ether was evaporated in vacuo and 25 mL of dry, deoxygenated toluene added to the residue. Finally, 1.5 g (18 mmol) of 1-hexyne was slowly added to the toluene suspension. After 2 h at 25 °C the reaction was heated for 45 min at 85 °C and insoluble salts were separated by filtration. The resulting solution of **6** was analyzed by hydrolysis: only *n*-hexane was found. Since the Cl_2AlH was used as its etherate, **6** was formed as its dietherate.

1,1-Bis(chloroethylalumino)hexane (7) was prepared by treating 1 molar equivalent of **6** in toluene with 1 molar equiv of neat

triethylaluminum and heating the resulting mixture at 50 °C for 60 min.

Typical Procedures for Methylenation. Bis(dichloroalumino)methane (1). A solution of 4.2 g (25 mmol) of BDAM was prepared by suspending BDAM in 80 mL of toluene at 10 °C and then adding 4.9 mL (60 mmol) of anhydrous THF. Thereupon, a solution of 4.0 g (22 mmol) of benzophenone in 10 mL of toluene was introduced and the mixture heated at reflux for 16 h. The hydrolytic workup as described above was followed (method A) to give 82% of chromatographically isolated 1,1-diphenylethylene (9).

Bis(chloroethylalumino)methane (3). A suspension of 5.2 g (25 mmol) of BDAM in 80 mL of methylene chloride at 10 °C was treated with 6.3 mL (60 mmol) of diethyl ether. After a solution resulted at 25 °C, the solution was recooled to 0 °C and treated with 3.4 mL (25 mmol) of triethylaluminum. A period of 30-min stirring at 25 °C was permitted before a solution of 3.8 g (22 mmol) of 4-phenylcyclohexanone in 15 mL of CH_2Cl_2 was added. The reaction was allowed to proceed for 3 h at 25 °C before a workup according to method A. A 75% yield of 4-phenyl-1-methylenecyclohexane was isolated by column chromatography.

For the reaction with 4-chromanone described below, poly-4-vinylpyridine was used to trap HCl evolved during hydrolysis. BDAM (2.60 g) was combined with ether (2 mL) and trimethylaluminum (1.0 mL). Then, 1.40 g of 4-chromanone was added. After a half-hour of stirring, the reaction mixture was quenched with poly-4-vinylpyridine and 0.1 M sodium hydroxide solution (1 mL) at 0 °C. The organic layer was separated from the polymer and the polymer was washed five times with 100 mL of ether. The organic layer and ether extracts were combined, washed with 0.1 M solution of NaOH, and dried over $MgSO_4$. The solvent was evaporated and 0.85 g of 2,3-dihydro-4-methylenebenzopyran was separated on a short basic alumina column (61% yield).

Bis(chloromethylalumino)methane (2). (a) From Trimethylaluminum. A suspension of 3.0 g (14 mmol) of BDAM in 30 mL of dry methylene chloride was cooled to 10 °C and treated with 3.2 mL (32 mmol) of diethyl ether. After a solution had been formed, 1.1 mL (15 mmol) of trimethylaluminum was added. The reaction mixture was stirred at 20–25 °C for 15 min and then 2.0 g (12 mmol) of 4-phenylcyclohexanone in 5 mL of CH_2Cl_2 was introduced. A distinct exotherm was observed. After 3 h of stirring at 20–25 °C, the reaction was worked up by method A to give 1.75 g (89%) of 4-phenyl-1-methylenecyclohexane.

(b) From Methylmagnesium Bromide. A suspension of 5.2 g (25 mmol) of BDAM in 80 mL of methylene chloride at 10 °C was treated with 6.3 mL (60 mmol) of diethyl ether. The mixture was stirred for 30 min at 25 °C to attain solution and then cooled to 10 °C. A 13.2-mL portion of 3 M methylmagnesium bromide in ether was then added. After 1 h of stirring, the suspension was filtered under nitrogen and the solid washed with methylene chloride (note: in some cases, centrifugation speeded up this operation). The concentrated filtrate (2.36% Al and 3.60% Cl) was apportioned for reaction.

Thus, 20 g of this solution reacted with 1.3 g (8.6 mmol) of dihydrocarvone. After 3 h of reaction and a workup by method A, a 95% yield of 4-(2-isopropenyl)-2-methyl-1-methylenecyclohexane was obtained.

(Dichloroalumino)(trichlorotitanio)methane (4). (a) Unmodified Reagent. A solution of 10.4 g (50 mmol) of BDAM in 95 mL of tetrahydrofuran was prepared slowly at 0 °C, because the dissolution is exothermic. Then the solution was brought to 25 °C and treated dropwise with a solution of 9.5 g (50 mmol) of titanium tetrachloride in 200 mL of THF. After 30 min at 55 °C the reaction mixture was concentrated to a red, semisolid residue under reduced pressure. The red residue was dissolved in toluene to give a final volume of the reagent as 250 mL.

Heating either 9 mmol of benzophenone or 9 mmol of 9-fluorenone with 50 mL of the titanium reagent at reflux for 30 min and then a hydrolytic workup by method A gave 100% of 1,1-diphenylethylene or 82% of 9-methylenefluorene, respectively.

(b) Modified Reagent and Workup for Isolating Enol Ethers. To 82 mL of the above methylenating agent were added 10 mmol of a 1:1 complex of methyl *p*-methylbenzoate and triethylaluminum (the latter complex being prepared by cautious admixing of the components at 0 °C) in 25 mL of toluene. The

(33) Wilke, G.; Müller, H. *Justus Liebigs Ann. Chem.* **1958**, *618*, 267.
(34) Finholt, A. E.; Bond, A. C.; Schlesinger, A. I. *J. Am. Chem. Soc.* **1947**, *69*, 1199.

reaction mixture was stirred for 72 h at 20–25 °C and then worked up by method B described above. An ¹H NMR spectral analysis of the reaction product showed the presence of a 3:7 ratio of methyl 1-*p*-tolylvinyl ether and the starting ester.

(c) Unmodified Agent Giving Aldol Condensation. Interaction of 100 mL of methylenating agent and 18 mmol of cyclohexanone gave, after 3 h at 25 °C and workup by method A, 60% of isolated 2-cyclohexylidenecyclohexanone, but no discernible methylene cyclohexane.

1,1-Dialuminohexanes (5–7) with Benzophenone. (a) Reagent 5. A solution of 18 mmol of 5 in 10 mL of toluene was mixed with a solution of 5.0 g (17.8 mmol) of benzophenone in 25 mL of anhydrous toluene. After 16 h of stirring at 25 °C, the reaction mixture was slowly and cautiously hydrolyzed (*gas evolution*) at 0 °C with 5 mL of 1 N aqueous HCl. The separated organic layer was washed with aqueous NaHCO₃, dried over anhydrous MgSO₄, and evaporated. Gas chromatographic analysis and mass spectral identification of the components showed that the ketone had been consumed, but only traces of the desired 1,1-diphenyl-1-heptene had been formed. The principal outcome

of the reaction was reduction: diphenylmethanol was separated and identified.

In another similar reaction, conducted for 17 h at 25 °C and for 60 min at 110 °C, a 9% yield of 1,1-diphenyl-1-heptene was obtained, but again reduction dominated. This finding suggests that the reduction to diphenylmethanol (as its aluminum salt) may be reversible.

(b) Reagent 6. In a reaction conducted in an analogous manner, this reagent converted benzophenone into 1,1-diphenyl-1-heptene in a 71% yield. This product could easily be separated from reduction products by column chromatography on silica gel with hexane as the eluent, or even by simple distillation. This hydrocarbon was identified by spectral comparison with an authentic sample that was obtained by the partial reduction of known 1,1-diphenyl-1,6-heptadiene.[35]

(c) Reagent 7. In a similar manner, after 16 h at 25 °C, 7 converted benzophenone into 1,1-diphenyl-1-heptene in 55% yield.

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(35) Eisch, J. J.; Merkley, J. H. *J. Am. Chem. Soc.* 1979, *101*, 1148.
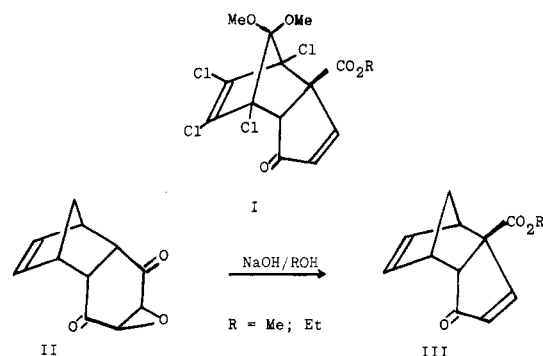

Notes

Base-Promoted Reaction of 5,6,7,8-Tetrachloro-5,8-dimethoxymethano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone Epoxide[1]

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In connection with our program aimed at the synthesis of homocubane and triquinane derivatives, we choose the tricyclic compound I as the starting material. The prep-

aration of I was suggested by the known reaction of tricyclic enedione epoxide II which, upon treatment with alcoholic sodium hydroxide, yielded the Favorskii ring contraction product III.[2] To this end, we undertook the investigation of the base-promoted reaction of the title compound 2. However, we found that the enedione epoxide 2 exhibited chemical behavior different from that

Scheme I[a]
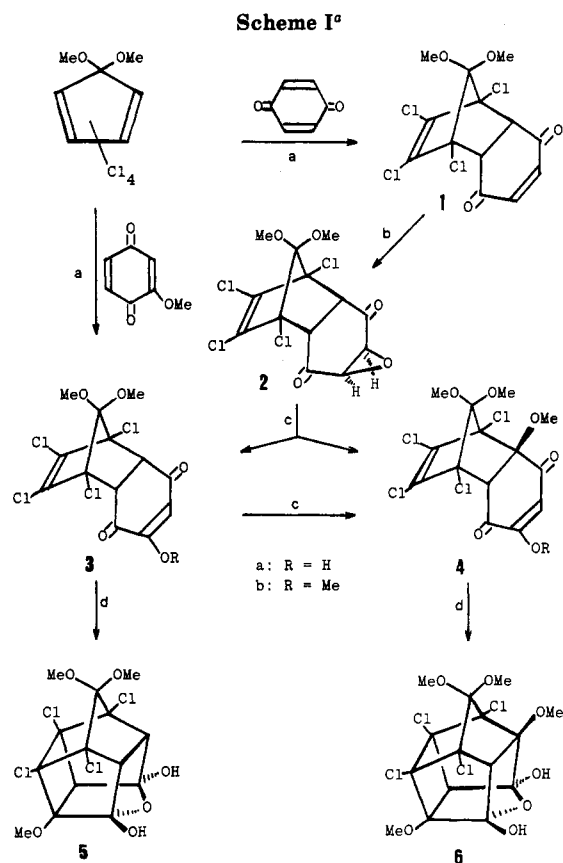
[a] (a) Benzene, reflux, ca. 2 days (3b, 98%); (b) acetone, ice-cold 20% aqueous NaHCO₃, 30% H₂O₂, 0 °C, 10 min (2, 95%); (c) NaOMe, MeOH, reflux, 2 h, then cold concentrated HCl (3a: 70%)/CH₂N₂, Et₂O (3b, 83%)//2 M aqueous NaOH, MeOH, overnight at room temperature, then cold concentrated HCl (4a, 70%)/CH₂N₂, Et₂O (4b, 88%); (d) acetone, light, 2 h (5, 73%; 6, 81%).

of epoxide II. In the present report, we describe the results of the study outlined in Scheme I.

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(1) Studies on Cage Compounds. 2. 1: Chou, T.-C.; Chiou, J.-H. *J. Chin. Chem. Soc.* 1986, *33*, 227.

(2) (a) Herz, W.; Iyer, V. S.; Nair, M. G. *J. Org. Chem.* 1975, *40*, 3519. (b) Marchand, A. P.; Suri, S. C. *Ibid.* 1984, *49*, 2041. (c) Klunder, A. J. H.; de Valk, W. C. G. M.; Verlaak, J. M. J.; Schellekens, J. W. M.; Noordik, J. H.; Parthasarathi, V.; Zwanenburg, B. *Tetrahedron* 1985, *41*, 963.