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PHOTOCHEMICAL POLAR ADDITION OF TRIALKYLBORANES

N. MIYAMOTO,* S. ISIYAMA, K. UTIMOTO and H. NOZAKI
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

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Abstract—*cis*-2-Alkylcyclohexanols are obtained stereoselectively upon irradiation of a mixture of cyclohexene and the corresponding trialkylborane in the presence of *p*-xylene as a sensitizer and upon the successive oxidation of the photolysate with alkaline H_2O_2. The similar reaction of 1-ethylcyclohexene yields 2,2-dialkylcyclohexanols. Cycloheptene also reacts with the boranes to afford *cis*-2-alkylcycloheptanols. These reactions are explained by assuming the highly strained *trans*-cyclohexene or -heptene to be the reactive species. Photochemically produced *trans*-cyclo-oct-2-enone and *cis,trans*-cyclo-octa-2,7-dienone react thermally with the bora e to give 3-alkylcyclo-octanone and *cis*-7-alkylcyclo-oct-2-enone, respectively. Photoreactions of acridine with the boranes result in reductive alkylation, affording 9-alkylacridans in fairly good yields.

Photochemical polar addition reactions have been recorded with such substrates as cycloalkenes,[1] conjugated cycloalkenones,[2] dienones[3] and benzopyridines[4] dissolved in protic media. The present report describes a novel photochemical addition of trialkylboranes to these substrates, providing a new synthesis of difficulty accessible compounds.†

Photoreaction of cyclohexene or -heptene with trialkylboranes. Recent studies[1] have shown that photosensitized excitation of cyclohexene or cycloheptene in protic solvents results in protonation of the olefin in the Markovnikov sense. The proposed reactive species is a highly strained, nucleophilic *trans*-cyclohexene or -cycloheptene. We wanted to examine the behaviour of this species as a strong base towards a trialkylborane.

A solution of cyclohexene and a trialkylborane (**1a–c**) dissolved in benzene-*p*-xylene was irradiated‡ and the photolysate was oxidized with alkaline H_2O_2. Work-up gave the corresponding *cis*-2-alkylcyclohexanols (**6p**) selectively, as shown in Table 1. The same reaction of 1-ethylcyclohexene with the boranes **1a** and **1b** gave 2,2-dialkylcyclohexanols (**6aq** and **6bq**), which were transformed into the corresponding 2,2-dialkylcyclohexanones (**9aq** and **9bq**). Cycloheptene also reacted with the borane **1a** and **1b** under the same irradiation conditions to afford *cis*-2-alkylcycloheptanols (**6ap′** and **6bp′**) selectively. The *cis*-2-alkylcyclohexanols (**6p**) were identified by comparison with the authentic samples synthesized following Scheme 1. Hydroboration[8] of **2** afforded *trans*-2-alkylcyclohexanols (**7**), which were oxidized to cyclohexanones (**8**). Hydride reduction of each ketone gave rise to a *cis-trans* mixture of the corresponding 2-alkylcyclohexanol. GLC analyses indicated that each photochemically produced alcohol was homogeneous and had the *cis*-configuration. The cyclohexanols **6aq** and **6bq** were oxidized to the corresponding cyclohexanones **9**, which were identical with those elaborately synthesized *via* alkylation§ of 2-ethylcyclohexanone. 2-Alkylcycloheptanols were similarly prepared.

Incidentally, asymmetric photoreaction of cyclohexene has been brought about by means of di-*n*-butylborinic (1*S*)-menthoxyacetic anhydride (**10**), which was readily obtained from **1b** and (1*S*)-menthoxyacetic acid.[10] Irradiation of a mixture of cyclohexene and **10** and subsequent oxidation, furnished an optically active alcohol (**6bp**, $[\alpha]_D^{20°}$ $-6{\cdot}2°$, $c = 0{\cdot}26$, EtOH, 15% e.e.) in 12% yield. The enantiomeric excess was determined by the NMR method employing tris[3-(tert-butylhydroxymethylene)-*d*-camphorato]europium(III) (**11**)[11] (Fig 1).

Systems involving either tricyclohexyl- and triisopropylborane or cyclopentene, cyclo-octene and cyclododecene as reaction components did not react similarly. This is reminiscent of the photochemistry of cyclo-olefins[1] in protic media; very probably *trans*-cyclohexene (**3**) or -cycloheptene is the common reactive species, which captures¶ the strong Lewis acid **1** to give a zwitterion **4**.

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†Part of this work has been published in a preliminary form.[5]

‡Light was consumed by benzene or *p*-xylene, since the borane and cycloalkenes do not absorb light of excitation wave length (mainly 254 nm).

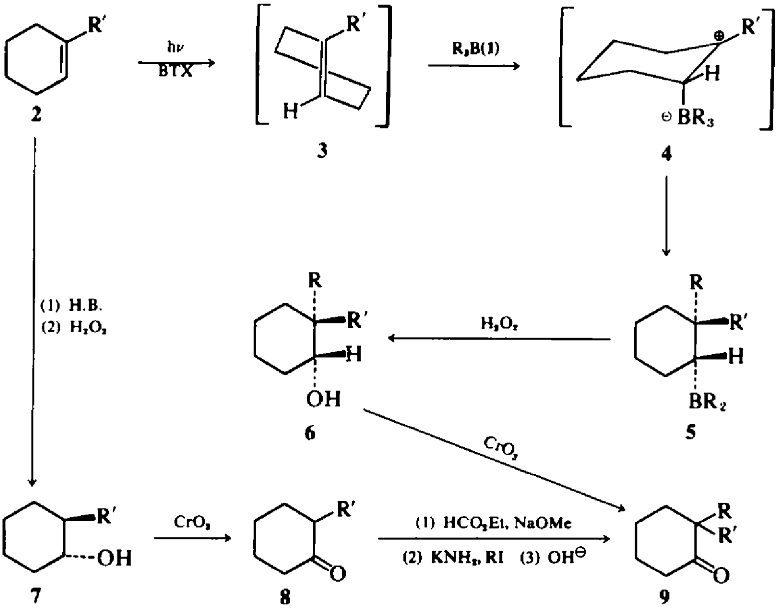
§This was attained by the alkylation of sodio 2-formyl-6-ethylcyclohexanone according to the method of Hauser *et al.*[9]

¶The driving force for this acid-base reaction is ascribed to strain-relief on the highly twisted olefinic bond occurring as in protonation to the photochemically-produced **3**.

Table 1. *cis*-2-Alkylcycloalkanols

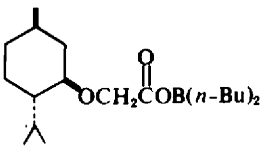
Compound	R	R'	yield (%)[a]	b.p. (°/mm)
6ap[b]	ethyl	H	86	95–100/20
6bp[c]	*n*-butyl	H	80	120–123/23
6cp	3-methoxypropyl	H	55	100–103/5·0
6aq	ethyl	ethyl	71	135–140/20
6bq	*n*-butyl	ethyl	68	138–145/20
6ap'[d]	ethyl	H	10	105–110/5·0
6bp'[d]	*n*-butyl	H	18	113–120/5·0

[a]Based on the borane **1**. [b]See ref. 6. [c]See ref. 7. [d]These refer to cycloheptene adducts.



R = (a) Et, (b) *n*-Bu, (c) 3-methoxypropyl, (d) *i*-Pr, (e) cyclohexyl.
R' = (p) H, (q) Et, (r) *n*-Bu, (s) 3-methoxypropyl.

SCHEME 1



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Migration of an alkyl anion occurs from boron to the electron-deficient carbon by the shortest path to result in the observed *cis* addition (Scheme 1).

This mechanism is supported by the observed stereospecific *cis* addition of the boranes **1**, and the regiospecific addition to the 1-ethylcyclohexene, and by the successful asymmetric synthesis of the alcohol **6bp**. The free radical mechanism is excluded. The reaction provides a new route to *cis*-2-alkylcyclohexanols, 2-alkylcyclohexanones, and 2,2-dialkylcyclohexanones.

Reaction of trialkylboranes with photochemically produced trans-*cyclo-oct-2-enone and* cis,trans-*cyclo-octa-2,7-dienone.* The fate of photochemically produced *trans*-cyclo-oct-2-enone (**14**)[2] and *cis,trans*-cyclo-octa-2,7-dienone (**19**)[3] is well documented.

An ethereal solution of *trans*-cyclo-oct-2-enone was produced by irradiating the *cis* isomer (**12**) at −78°.[2] The light source was turned off and the borane **1a** was added. After warming up to room temperature, the resulting mixture was hydrolysed to give 3-ethylcyclo-octanone (**13a**, 70%*). A simi-

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*All yields given hereafter are based on the unsaturated substrates initially employed, without consideration of recoverable starting material.

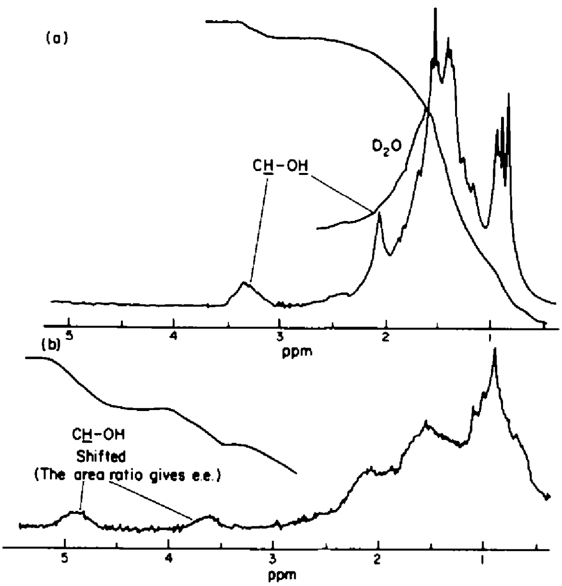


Fig 1. NMR spectra of (a) optically active *cis*-2-butylcyclohexanol obtained photochemically (**6bp**, 0·090 mmol) in CCl_4 (0·40 ml) and (b) the alcohol (**6bp**, 0·081 mmol) in CCl_4 (0·40 ml) containing the shift reagent (**11**, 0·016 mmol).

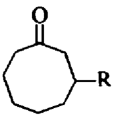
lar reaction with the borane **1d** furnished 3-isopropylcyclo-octanone (**13d**, 83%). These products were also obtained by the known addition of the borane to the enone **12** induced photochemically[12] or by oxygen catalysis.[13] When an ethereal solution of the enone **12** and the borane **1a** or **1b** was allowed to stand in the dark, the adducts were produced in smaller yields; 5·0% of **13a** and 8·4% of **13d**. An ethereal solution of *cis,cis*-cyclo-octa-2,7-dienone (**15**) was irradiated at -78°[3] and the resulting mixture of **15** and *cis,trans*-dienone **19** was treated with the borane **1a** or **1d** similarly to afford 7-ethylcyclo-oct-2-enone (**16a**, 15%) and 7-isopropylcyclo-oct-2-enone (**16d**, 23%), respectively. Irradiation of an ethereal solution of the dienone **15** and the borane **1a** or **1d** followed by hydrolysis afforded the enone **16a** or **16d**, respectively, as a single product. On the other hand, oxygen-initiated reaction of the dienone **15** with either the borane **1a** or **1d** dissolved in THF–H_2O gave a mixture of the enone (**16a** or **16d**) and the double adduct (**17a** or **17d**). The saturated ketones **17** were found to be *trans*-3,7-dialkylcyclo-octanones on the basis that the hydride-reduction yielded a single reduction product **18*** in each case.

Meanwhile, an ethereal solution of the dienone **15** and the borane **1a** or **1d** was kept in the dark to result in the complete recovery of the dienone **15**.

The observed reactivity of the pre-irradiated enone **12** and dienone **15** is attributed to such reactive species as *trans*-cyclo-oct-2-enone (**14**) and *cis,trans*-cyclo-octa-2,7-dienone (**19**), which are both key intermediates in the protic solvent incorporation.[2,3] The attack of the strained enone and dienone system by the Lewis acid **1** would be followed by the migration of the alkyl anion to the electron-deficient β-carbon.

Photochemical and thermal reaction of acridine with trialkylboranes. Finally, the photoreaction of acridine and its derivatives[4] with trialkylboranes has been studied. Irradiation of a mixture of acridine and the borane **1a** dissolved in benzene or *n*-hexane gave 9-ethylacridan[4] (**20a**, 72%) and 9-ethylacridine[4] (**23a**, 6·0%) besides 9,9′-biacridan (**24**, 3·0%) (Scheme 2). The similar reaction with the borane **1b**, **1d** or **1e** yielded 9-*n*-butylacridan[4] (**20b**, 65%), 9-*n*-butylacridine[4] (**23b**, 8·0%) and **24** (3·0%); 9-isopropylacridan (**20d**, 86%), 9-isopropylacridine (**23d**, 3·0%) and **24** (4·0%); 9-cyclohexylacridan[14] (**20e**, 90%), 9-cyclohexylacridine[14] (**23e**, 5·0%) and **24** (2·0%).

Allowing the mixture of acridine and the borane **1b** to stand at room temperature gave 9-alkylated acridan **20b** (10%). Thus the addition is definitely accelerated by irradiation. The enhanced reactivity of acridine upon irradiation is ascribed to the



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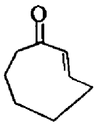

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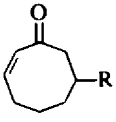

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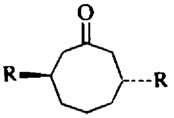

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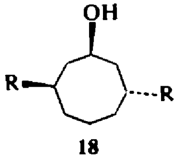

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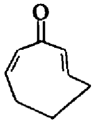

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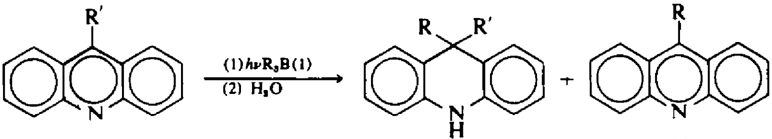
*The homogeneity of the alcohols **18a** and **18d** was established by GLC analyses on a capillary column (BDS 45 m, 110°).



R′ = H (**20**),
Me (**21**),
Et (**22**)

23

SCHEME 2

increased basicity* of the excited state. In sharp contrast to the photochemical reaction of cyclohexene or cycloheptene, the thermal reaction of acridine with the boranes having secondary alkyl groups such as **1d** or **1e** proceeded much more readily than those with primary alkyl substituents such as **1a** or **1b** to produce high yields of 9-alkylated acridans such as **20d** (90%) and **20e** (75%). Thus the boranes are convenient means† for introducing an α-branched alkyl group at the 9-position of acridine either thermally or photochemically. Irradiation of 9-alkylacridines with the appropriate borane gives rise to 9,9-dialkylated acridans. This is exemplified by the photoreaction of 9-ethylacridine with the borane **1a** giving 9,9-diethylacridan[4] (**22a**, 72%). Similarly, the borane **1a** with 9-methylacridine[4] produced 9-ethyl-9-methylacridan[4] (**21a**, 75%) photochemically.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were obtained on a Shimazu IR-27-G spectrometer in liquid film unless otherwise stated. NMR spectra were taken with a JEOL C-60-H spectrometer (60 MHz) with CCl_4 as a solvent and chemical shifts are recorded in δ values relative to TMS as an internal standard. NMR data are given in the order of multiplicity (*s* = singlet, *d* = doublet, *t* = triplet and *m* = unresolved multiplet), integration and assignment. UV spectra were taken in EtOH on a Hitachi EPS-2 recording spectrometer. Optical rotations were measured in EtOH solutions with a 5 cm cell. Column chromatography was carried out on Mallinckrodt silicic acid (100 mesh). Plates of silica gel G were used for TLC and the spots were visualized with iodine vapour.

Irradiation of a benzene solution of cycloalkene, trialkylborane and p-*xylene*

A soln of cycloalkene (**2** or **2′**,‡ 15 mmol) and the borane (**1**, 5·0 mmol) dissolved in benzene (70 ml) containing *p*-xylene (5·0 ml) was placed in a quartz vessel and irradiated externally by means of 200 W high pressure mercury arc under nitrogen atmosphere at room temp for 48 h. The progress of the reaction was followed by GLC analyses (HVSG 10%, 2 m, 130°) of aliquots after oxidation with alkaline (3N NaOH) H_2O_2. The reaction mixture was treated with alkaline H_2O_2 and the resulting solution was extracted twice with ether. The combined extracts were washed with brine and then dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed over silica gel. Elution with benzene–ether (1 : 1) gave the crude alcohol **6** or **6′**, which was distilled to afford analytically pure material.

The photoreaction of cyclohexene with tri(3-methoxypropyl)borane (**1c**) was performed in the following manner. To 3-methoxypropene (1·1 g, 15 mmol) in THF (5·0 ml) was added with stirring BH_3 (5·0 mmol) in THF (3·5 ml) at 0° under nitrogen. The soln was stirred at room temp for 3 h. After removal of THF *in vacuo*, the crude mixture§ of **1c** (83%) and tri(1-methoxy-2-propyl)borane (15%) was added to cyclohexene (1·2 g, 15 mmol) in benzene (70 ml) containing *p*-xylene (5·0 ml). Irradiation and work-up gave **6cp**. The results are given in Table 1.

*Irradiation of a benzene solution of cyclohexene, di-*n-*butylborinic (1S)-menthoxyacetic anhydride* (**10**) *and* p-*xylene*

To the borane (**1b**, 910 mg, 5·0 mmol) was added slowly with stirring (1*S*)-menthoxyacetic acid[18] at room temp under nitrogen according to the method reported by Meerwein[10] for the preparation of diethylborinic acetic anhydride. Spontaneous evolution of *n*-butane under exothermic reaction was observed during the addition of the acid. The resulting mixture was heated at 70° for 1 h. The crude borinic anhydride **10** was immediately added to a benzene (70 ml) soln of cyclohexene (1·2 g, 15 mmol) and *p*-xylene (5·0 ml) in a quartz vessel under nitrogen. The irradiation for 72 h afforded the optically active alcohol (**6bp**, 12% based on **1b** used), which was purified by preparative GLC (Apiezon 30%, 1 m, 150°). The enantiomeric excess of **6bp** is given above.

Independent syntheses of cis-*2-alkylcycloalkanols* (**6p**, **6p′**). (a) *2-Alkylcycloalkanones* (**8**, **8′**)

The *trans*-alcohols **7** and **7′** prepared *via* hydroboration of the olefins **2** and **2′** and the successive treatment with alkaline H_2O_2 were oxidized with Jones reagent. Distillation afforded the corresponding ketones **8** and **8′**. The ketone **8s** was prepared as follows. A soln of cyclohexene (3·0 g, 31 mmol) in dry ether (5·0 ml) was added dropwise to the Grignard reagent prepared from 3-methoxypropyl-1-bromide[16] and Mg (74 mg, 31 mmol) activated with a small amount of iodine in dry ether (10 ml) in the course of 30 min. After the soln was stirred

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*Benzopyridines show marked enhancement of the basicity in the first excited singlet state.[15]

†Other heteroaromatics such as quinoline, isoquinoline or indole fail to react with the borane **1** either photochemically or thermally.

‡The sign ′ refers to the seven-membered ring system.

§After hydroboration, the reaction mixture was oxidized with alkaline H_2O_2 to give 3-methoxypropan-1-ol[16] (83%), 1-methoxy-propan-2-ol[17] (15%) and propan-1-ol (2·0%). The crude mixture of **1c** (83%) and tri(1-methoxy-2-propyl)borane (15%) was subjected to the successive photoreaction, since the boranes having secondary alkyls failed to react with cyclohexene as shown in the discussion part.

under reflux for 3 h, the reaction mixture was decomposed with aq NH$_4$Cl. Ether extraction and drying (Na$_2$SO$_4$) followed by concentration afforded 1-(3-methoxypropyl)cyclohexan-1-ol as a light yellow oil. The mixture of the crude alcohol and H$_3$PO$_4$ (1·0 ml) was heated at 130° for 2 h. Extraction with ether, drying (Na$_2$SO$_4$) and concentration *in vacuo* followed by distillation afforded 1-(3-methoxypropyl)cyclohex-1-ene (**2s**, 2·9 g, 62% based on cyclohexanone), b.p. 70–73°/20 mm, which was purified by preparative GLC (HVSG 30%, 2 m, 85°).

2-(3-methoxypropyl)cyclohexanone (**8s**) was prepared *via* hydroboration of the olefin **2s** and the subsequent oxidation of the alcohol **7s** as shown above. The results are given in the order of the kind of the ketone, b.p. (°/mm) and yield (%). **8q**,[19] 70–75/22, 83; **8r**,[20] 110–115/25, 75; **8s**, 75–77/5·0, 87; **8q′**,[21] 90–93/22, 90; **8r′**,[22] 135–140/7·0, 74.

(b) *Hydride-reduction of 2-alkylcycloalkanones* **8** *and* **8′**. The ketone (**8** or **8′**, 10 mmol) dissolved in dry ether (5·0 ml) was added slowly with stirring to LAH (110 mg, 3·0 mmol) in dry ether (5·0 ml). After the reaction mixture was decomposed with aq Na$_2$SO$_4$. The ether layer was dried (Na$_2$SO$_4$), concentrated *in vacuo* and distilled to give the isomeric mixture of the *trans*-alcohol (**7** or **7′**) and *cis*-one (**6p** or **6p′**). The two isomers were separated on a capillary column (BDS 45 m × 0·50 mm i.d., 100°), where the *trans* isomer **7** or **7′** was identified by comparison of the retention time with the one of specimen prepared *via* hydroboration of the olefin **2** or **2′**. The results are given in the order of the kind of the alcohols, the *cis/trans* ratio and yield (%). **6ap** and **7q**, 2/3, 85; **6bp** and **7r**, 2/3, 87; **6cp** and **7s**, 2/3, 91; **6ap′** and **7q′**, 4/5, 78; **6bp′** and **7r′**, 4/5, 82. Thus the alcohol formed in every photoreaction was ascertained to be *cis*.

Oxidation of the photoproducts **6aq** *and* **6bq** *to the ketones* **9aq** *and* **9bq**. The oxidation of **6aq** and **6bq** afforded the corresponding ketones **9aq**[23] (b.p. 95–100°/20 mm, 73%) and **9bq**[23] (123–125/20, 82).

Independent syntheses of the ketones **9aq** *and* **9bq**. The method was based on Hauser *et al*[9] and work-up followed by distillation gave the ketones (**9aq**,[23] 48% based on sodio formyl ketone), **9bq**[23] (63%).

Reaction of cyclo-oct-2-enone **12** *with the borane* **1** *under various conditions*

Condition A: *Thermal reaction of the photochemically produced* trans-*enone* **14** *with the borane* **1**. The *trans*-enone **14** dissolved in ether was photochemically produced according to the method reported by Noyori.[2] An ethereal soln (20 ml) of *cis*-cyclo-oct-2-enone[24] (**12**, 500 mg, 4·0 mmol, $\lambda_{max} = 310$ nm, $\log \epsilon = 1{\cdot}90$) was placed in a Pyrex vessel and irradiated externally by means of 200 W high pressure mercury arc under nitrogen at −78° for 15 min. After the light source was turned off, the borane (**1**, 4·4 mmol) was immediately added to the photolysate. Upon warming up to room temp, the resulting soln was treated with trimethylamine oxide[25] to decompose the excess of the borane **1**. Hydrolysis followed by usual work-up gave 3-alkylcyclo-octanone (**13**) along with unchanged enone **12**.

Table 2. Physical properties of new compounds in cycloalkene reaction

No	IR (cm^{-1})	NMR (δ, ppm)
6cp	3400, 1010	2·20(*s*, 1H, —OH), 2·53(*t*, 2H, —C$\underline{H}_2$OCH$_3$), 3·20(*s*, 3H, —OCH$_3$), 3·60(*m*, 1H, —C$\underline{H}$OH—)
6aq	3400, 1020	1·90(*s*, 1H, —OH), 3·40(*m*, 1H, —C$\underline{H}$OH—)
6bq	3400, 1020	1·92(*s*, 1H, —OH), 3·50(*m*, 1H, —C$\underline{H}$OH—)
6ap′	3400, 1015	2·10(*s*, 1H, —OH), 3·48(*m*, 1H, —C$\underline{H}$OH—)
6bp′	3400, 1015	1·95(*s*, 1H, —OH), 3·33(*m*, 1H, —C$\underline{H}$OH—)
2s	1110	2·50(*t*, 2H, —C$\underline{H}_2$OCH$_3$), 3·21(*s*, 3H, —OCH$_3$), 5·35(*m*, 1H, vinylic)
8s	1710, 1110	2·20–2·50(*m*, 2H, —CH$_2$—C═O), 2·51(*t*, 2H, —C$\underline{H}_2$OCH$_3$), 3·21(*s*, 3H, —OCH$_3$), 3·30 (*t*, 1H, methine)

Table 3. Reaction of the enone **12** or the dienone **15** with the borane **1**

borane	product	b.p. (°/mm)	condition (yield, %)
1a	**13a**	98–100/5·0	A (70), B (72), C (52), D[a] (5·0)
1d	**13d**	100–103/5·0	A (83), B (80), C (64), D[a] (8·4)
1a	**16a**	93–98/4·0	A[b] (15), B (78), D[c] (0·0)
	16a, 17a	100–105/0·10[d]	C (23, 33)
1d	**16d**	102–108/4·0	A[b] (23), B (82), D[c] (0·0)
	16d, 17d	95–101/0·050[e]	C (36, 28)

[a] The enone (**12**, 90–95%) was recovered on the basis of **12** used.

[b] The dienone (**15**, 75–85%) was recovered on the basis of **15** used.

[c] The GLC analyses (HVSG 20%, 2m, 180°) revealed the complete recovery of **15**.

[d] B.p. of **17a**.

[e] B.p. of **17d**.

Table 4. Physical properties of new compounds in cyclo-octenone and -octadienone

No	IR (cm^{-1})	NMR (δ, ppm)
13a	1700	0·98(t, 3H, —CH_3), 2·10–2·35(m, 4H, CH_2 adjacent to C=O)
13d	1700	0·95(d, 6H, —CH_3), 2·10–2·33(m, 4H, CH_2 adjacent to C=O)
16a	1660	1·00(t, 3H, —CH_3), 2·52–2·57(m, 4H, CH_2 adjacent to sp^2 carbon), 5·93–6·50(m, 2H, vinylic)
16d	1660	0·99(d, 6H, —CH_3), 2·51–2·58(m, 4H, CH_2 adjacent to sp^2 carbon), 5·93–6·50(m, 2H, vinylic)
17a	1710	0·99(t, 6H, —CH_3), 2·11–2·58(m, 4H, CH_2 adjacent to C=O)
17d	1720	0·95(d, 12H, —CH_3), 2·10–2·40(m. 4H, CH_2 adjacent to C=O)

Table 5. Elemental analyses of all new compounds

		Required, %		Found, %	
No	Formula	C	H	C	H
6cp	$C_{10}H_{20}O_2$	69·7	11·7	69·3	11·7
6aq	$C_{10}H_{20}O$	76·9	12·9	76·6	12·7
6bq	$C_{12}H_{24}O$	78·2	13·1	78·5	13·3
6ap′	$C_9H_{18}O$	76·0	12·8	76·3	12·4
6bp′	$C_{11}H_{22}O$	77·6	13·6	77·2	13·2
2s	$C_{10}H_{18}O$	77·9	11·8	77·5	11·5
8s	$C_{10}H_{18}O_2$	70·5	10·7	70·9	10·8
13a	$C_{10}H_{18}O$	77·9	11·8	77·5	11·6
13d	$C_{11}H_{20}O$	78·5	12·0	78·9	12·3
16a	$C_{10}H_{16}O$	78·9	10·6	79·2	10·6
16d	$C_{11}H_{18}O$	79·5	11·0	79·2	11·0
17a	$C_{12}H_{22}O$	79·1	12·2	79·4	12·0
17d	$C_{14}H_{26}O$	80·0	12·5	79·6	12·4
18a	$C_{12}H_{24}O$	78·2	13·1	78·4	12·9
18d	$C_{14}H_{26}O$	80·0	12·5	79·5	12·4
20d	$C_{16}H_{17}N$[a]	86·1	7·7	85·9	7·5
23d	$C_{16}H_{15}N$[b]	86·8	6·8	87·0	6·9

[a] Required: N, 6·3. Found: N, 6·0%. [b] Required: N, 6·3. Found: N, 5·8%.

Condition B: *Irradiation of an ethereal solution of the enone* **12** *with the borane* **1**. A soln of the enone (**12**, 500 mg, 4·0 mmol) and the borane (**1**, 4·4 mmol) in ether (20 ml) was placed in a Pyrex vessel and irradiated externally by means of 200 W high pressure mercury arc under nitrogen for 2 h. Work-up as above afforded the ketone **13**.

Condition C: *oxygen-induced reaction of the enone* **12** *with the borane* **1**. The method was based on one reported by Brown *et al.*[13] The enone (**12**, 500 mg, 4·0 mmol) in THF (10 ml) was treated with H_2O (0·50 ml) and then with the borane (**1**, 4·4 mmol) under nitrogen. Then air was passed into the flask at a rate of 1–5 ml/min through a syringe needle placed through the rubber septum cap to a point just above the reaction mixture. The similar work-up as above gave the ketone **13**.

Condition D: *Dark reaction of the enone* **12** *with the borane* **1** *under nitrogen*. An ethereal soln (20 ml) of the enone (**12**, 500 mg, 4·0 mmol) and the borane (**1**, 4·4 mmol) was allowed to stand in the dark under nitrogen at room temp for 24 h.

The reaction of *cis,cis*-cyclo-octa-2,7-dienone[24] (**15**, λ_{max} = 353 nm, log ϵ = 1·79) with the borane **1** was performed under the same conditions for enone **12**. The results are summarized in Table 3.

Hydride-reduction of the ketone **17**

The ketone (**17**, 3·0 mmol) was reduced to the alcohol **18** with LAH (34 mg, 0·90 mmol). **18a**: b.p. 103–110°/0·050 mm, 92%, IR 3400 and 1025 cm^{-1}, NMR δ 0·99 (t, 6H, —CH_3), 2·01 (s, 1H, —OH) and 3·43 ppm (m, 1H, —C$\underline{\text{H}}$OH—). **18d**: b.p. 122–130°/0·010 mm, 85%, IR 3400 and 1023 cm^{-1}, NMR δ 0·96 (d, 12H, —CH_3), 2·00 (s, 1H, —OH) and 3·40 ppm (m, 1H, —C$\underline{\text{H}}$OH—).

The homogeneity of each alcohol **18** was established by GLC analyses on a capillary column (BDS 45 m, 110°).

Photochemical and thermal reaction of acridine and its 9-alkylated derivatives with the borane **1**

A soln of acridine or its derivatives (5·0 mmol) and the borane (**1**, 5·1 mmol) dissolved in benzene or hexane (70 ml) was placed in a Pyrex vessel and irradiated externally by means of 200 W high pressure mercury arc under nitrogen atmosphere at room temp for 48 h. The progress of the reaction was followed by TLC analyses of aliquots. After a ppt of biacridan was filtered off, the filtrate was treated with alkaline H_2O_2 to decompose the excess of the borane **1**. Extraction with ether, drying (Na_2SO_4) and concentration *in vacuo* followed by column chromatography on silica gel (benzene elution) afforded the alkylated acridan together with the alkylated acridine.

A benzene or hexane solution (70 ml) of acridine (5·0 mmol) and the borane (**1**, 5·1 mmol) was allowed to stand in the dark under nitrogen at room temp for 72 h. Work-up as above followed by column chromatography yielded the alkylated acridan as well as the recovered acridine. The physical properties of the hitherto-unknown compounds are shown as follows. **20d**: m.p. 156–157° (from hexane), IR (KBr) 3370, 1605 and 750 cm^{-1}, NMR δ 0·75 (d, 6H, —CH_3), 3·70 (d, 1H, C(9)H), 5·90 (s, 1H, —NH—) and 6·60–7·10 ppm (m, 8H, aromatic). **23d**: m.p. 65–66° (from hexane), IR (KBr) 1605 and 750 cm^{-1}. NMR δ 1·38 (d, 6H, —CH_3), 5·50 (m, 1H, methine) and 7·10–8·20 ppm (m, 8H, aromatic).

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