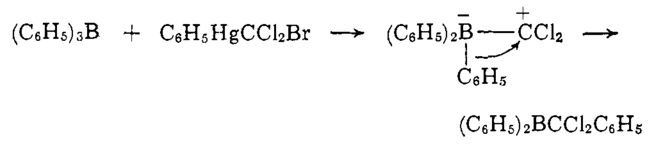
octene) were obtained when $C_6H_5HgCCl_2Br$ (30.9 mmoles) was allowed to react with a mixture of 15.4 mmoles each of tri-*n*-propyl- and tri-*n*-butylborane. It may be noted that decarboxylation of sodium trichloroacetate in the presence of tri-*n*-propylborane also gave 3-heptene (*cis*/*trans* = 1.56), but the yield was only 15%.

The initially formed $RCCl_2B<$ products appeared to be more stable in the case of arylboranes. With triphenylborane a dark reaction mixture was formed when it was heated at *ca.* 60° in benzene for 1 hr with an equimolar quantity of $C_6H_5HgCCl_2Br$. Addition of an excess of cyclohexene and further heating at reflux for 16 hr followed. The major volatile products were 7-chloro-7-phenylnorcarane (21.4% yield, a mixture of the *exo* and *endo* isomers) and trichlorostyrene ($C_6H_5CCl{=}CCl_2$; 35% yield). The products obtained can be rationalized in terms of initial CCl_2 transfer to boron followed by B to C phenyl migration.

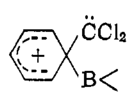


$$(C_6H_5)_3B + C_6H_5HgCCl_2Br \longrightarrow (C_6H_5)_2\underset{C_6H_5}{\overset{-}{B}}—\overset{+}{C}Cl_2 \longrightarrow (C_6H_5)_2BCCl_2C_6H_5$$

Reaction of the α,α-dichlorobenzylboron intermediate with cyclohexene, either in a bimolecular process or *via* α elimination to give phenylchlorocarbene, would produce 7-chloro-7-phenylnorcarane. The formation of trichlorostyrene is best explained by further CCl_2 "insertion" into the $C_6H_5CCl_2$–B linkage to give the $>BCCl_2CCl_2C_6H_5$ system, which in analogy to the known chemistry of (β-chloroalkyl)boron compounds[11,12] should undergo facile β elimination ($\rightarrow >B—Cl + Cl_2C{=}CClC_6H_5$). Formation of trichlorostyrene must have been complete by the time the $C_6H_5HgCCl_2Br$ was consumed and prior to the addition of cyclohexene, since 7,7-dichloronorcarane was not among the reaction products. Attempts to isolate an intermediate α,α-dichlorobenzylborane were not successful. However, it was found that tris(α,α-dichlorobenzyl)borane (prepared *in situ* by reaction of boron trifluoride etherate and α,α-dichlorobenzyllithium[13]) reacted with 3 molar equiv of phenyl(bromodichloromethyl)mercury in benzene at reflux to give trichlorostyrene in fair yield.

An experiment in which phenyldimethoxyborane and $C_6H_5HgCCl_2Br$ were allowed to react in benzene at 60–70° and the resulting reaction mixture then was heated with cyclohexene at reflux for 20 hr produced 7-chloro-7-phenylnorcarane (27.3%), trichlorostyrene (22.4%), and 1,2-dichloro-1-methoxy-2-phenylethylene ($C_6H_5CCl{=}CClOCH_3$; 34.7%). The formation of the latter implies that after CCl_2 attack at boron both phenyl and methoxy groups migrate from boron to carbon, giving $C_6H_5CCl_2B<$ and $CH_3OCCl_2B<$ intermediates. The absence of 7-chloro-7-methoxynorcarane among the products suggests that the methoxydichloromethylborane intermediate is less stable than the α,α-dichlorobenzylboron species to the extent that, once formed, it decomposes immediately to give $CH_3O\ddot{C}Cl$ which then could "insert" into a $C_6H_5CCl_2$–B linkage. β elimination would then give the observed olefin.

The reactions occurring between $C_6H_5HgCCl_2Br$ and phenylboranes also could be rationalized in terms of electrophilic attack of CCl_2 at carbon to give III,



III

subsequent rearrangement of which could lead to the α,α-dichlorobenzylboron species. However, the fact that such reactions occur very readily with trialkylboranes, which are much less susceptible to electrophilic attack,[14] would tend to speak against this view.

Syntheses of novel olefins based on reactions of phenyl(trihalomethyl)mercurials with organoboranes are being investigated. We also find that use of an excess of $C_6H_5HgCCl_2Br$ in reactions with trialkylboranes allows direct synthesis of *gem*-dichlorocyclopropanes derived from the internal olefins produced. Details of this and related work will be reported at a later date.

Acknowledgment. The authors are grateful to the U. S. Army Research Office (Durham) for generous support of this work.

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(11) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

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(15) Alfred P. Sloan Foundation Fellow, 1962–1966.

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Received February 5, 1966

Novel Photocyclization of a Highly Phenylated β,γ-Unsaturated Ketone to a Cyclopropyl Ketone, Involving Benzoyl Group Migration

Sir:

The photolytic rearrangement of bis-(2,3,5,5-tetraphenyl-2-dihydrofuranyl)-1,2-hydrazine to 1,3,4,4-tetraphenyl-3-buten-1-one (III, 60%)[1] and its 1,2,4,4 isomer (I, 25%)[2] invited investigation of β,γ-unsaturated ketones themselves, and we report herewith the preliminary results and their significance relative to current photochemical literature.[3]

Among the products of irradiation[4] of the 1,2,4,4-tetraphenyl β,γ-unsaturated ketone I, we have isolated the cyclopropyl ketone II[5] consistently in *ca.* 7% yields.[5b]

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(1) (a) R. E. Lutz, J. I. Dale, and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963); (b) R. E. Lutz and C. L. Dickerson, *J. Org. Chem.*, **27**, 2041 (1962).

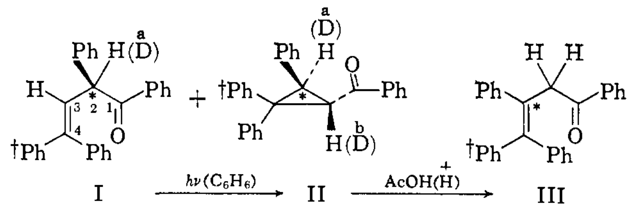
(2) (a) D. W. Boykin, Jr., and R. E. Lutz, *J. Am. Chem. Soc.*, **86**, 5046 (1964), ref 2a; (b) R. E. Lutz, R. G. Bass, and D. W. Boykin, Jr., *J. Org. Chem.*, **29**, 3660 (1964), ref 8; (c) D. W. Boykin, Jr., Ph.D. Dissertation, University of Virginia, 1965.

(3) (a) Photointerconversion of phenylated propenes and cyclopropanes: G. W. Griffin, *et al.*, *J. Am. Chem. Soc.*, **87**, 1410 (1965), ref 17; (b) *Tetrahedron Letters*, **34**, 2951 (1965); (c) photocyclization of desyl compounds: J. C. Sheehan and R. M. Wilson, *J. Am. Chem. Soc.*, **86**, 5277 (1964); (d) irradiation of 4-hexen-2-one with *trans–cis* inversion: H. Morrison, *Tetrahedron Letters*, **48**, 3653 (1964); (e) photocyclization of a γ,δ-unsaturated ketone: R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960); (f) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, **20**, 1525 (1965); (g) photocyclization of a β,γ-epoxyketone: A. Padwa, *J. Am. Chem. Soc.*, **87**, 4205 (1965).

(4) Hanovia high-pressure Hg arc lamp, Type L, 450 w, Pyrex filter; I in benzene (1.3 m*M*), under N_2, 1.5 hr.

(5) (a) II had been identified before we learned of Griffin's work,[3a] but at that time it had been erroneously assumed to stem from phenyl rather than benzoyl group migration. (b) The major products were noncrystalline. Compounds arising evidently from radical fragmentation (*cf.* VII) include biphenyl and dimeric hydrocarbons $C_{42}H_{34}$ (*ca.* 15%).

The structure is based on analysis, spectral data, acid-catalyzed rearrangement to the isomeric 1,3,4,4-tetraphenyl β,γ-unsaturated ketone III,[1] and independent synthesis by photocondensation of diphenyldiazomethane with *trans*-chalcone[2c] (20%). The *trans* configuration (II), tentatively assigned from nmr data[2c,6] and presumed from the mode of synthesis,[6b] was confirmed by base-catalyzed deuterium exchange for the α-hydrogen (to IIa) without stereoisomerization, which indicated the compound to be in its more stable form.



Ph = C_6H_5; a, b = deuterated; * or † = C-14 labeled

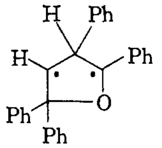
The formation of II and III from I empirically required migration, relative to I, of either the phenyl or the benzoyl group from C-2 to C-3. To determine which group had migrated, the unsaturated ketone I C^{14}-labeled at C-2 was prepared and photocyclized to the cyclopropyl ketone II*. Subsequent acid-catalyzed isomerization to ketone III* and permanganate oxidation to benzoic acid (containing 73% of the C^{14} label[7] of I*) and cold benzophenone (as the 2,4-DNP), showed that in the main the benzoyl group had migrated away from C-2 of I* and that the phenyl group had remained attached to that carbon.

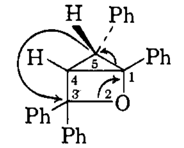
Since these results did not preclude the possibility that one of the C-4 phenyl groups of I had migrated, the ketone I† C^{14}-labeled in one of the C-4 phenyl groups was synthesized and photocyclized to II†. Isomerization to III† and oxidation to 77% C^{14}-labeled benzophenone[7] and cold benzoic acid proved that in the main migration of a 4-phenyl had not occurred.

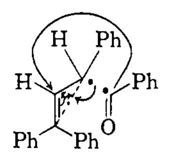
Additional evidence for migration of the benzoyl rather than the phenyl group appeared in the comparison of the nmr spectra of I and IIb (benzene) with that of deuterated ketone IIa from photocyclization of Ia. This showed that both the α-phenyl and α-D of I were retained on the same carbon in the cyclopropyl ketone IIa and that the benzoyl group had migrated and thus acquired a new α-H.

It is presumed[4] that the photocyclization I → II involves an initial n,π^* excited state. Consistent with this is the negative result of a comparable irradiation of the phenylcarbinol IV made by addition of phenyllithium to the ketone I, from which we failed to isolate the cyclopropylcarbinol of II.[2c]

The C^{14}-tracing experiments have excluded as principal mechanisms those involving a dihydrofuran intermediate (*cf.* ref 2) or any of the conceivable migrations of a phenyl group or hydrogen in the five-membered ring diradical V (*cf.* ref 3c) formed by the interaction of the excited carbonyl group and the double bond. The diradical V, however, could cyclize transannularly to bicyclotetrahydrofuran VI, a bicyclic oxetane, for which there is analogy in the actual isolation of the presumably less strained homologous bicyclotetrahydropyrans in photocyclization of γ,δ-unsaturated ketones[3e,f] (*cf.* the isolation of an isomeric bicyclotetrahydrofuran, a hydroxycyclobutane epoxide, in the photocyclization of a β,γ-epoxyketone[3g]). Bicyclic oxetane VI might collapse by valence tautomerization either with 1,4 bond cleavage to regenerate I, or by cleavage at the presumably weaker 1,5 bond to give the cyclopropyl ketone II.


V


VI


VII

Formation of biphenyl and relatively large amounts of $C_{42}H_{34}$[5b] from photolysis of I to benzoyl and triphenylallyl radicals, however, suggests a possibly indistinguishable alternative or competing recombination of these radicals, concertedly or in a solvent cage (VII), a mechanism without sure analogy but consistent with the C^{14}-tracing experiments.

Work is in progress on the generality and mechanism of these types of reactions, especially the importance of substituents which would favor or disfavor cyclopropyl ring formation and stability, or which would serve as leaving groups, thereby to effect furanization.[3c,8]

Data. I*: from $PhC^*H_2COOH \rightarrow PhC^*H_2COPh \rightarrow CH_2{=}C^*(Ph)COPh$, followed by photocondensation with Ph_2CN_2 to the cyclopropyl ketone and acid-catalyzed rearrangement. I†: by monoaddition of uniformly C^{14}-labeled Ph†MgBr to the unhindered carbonyl group of $PhCOCH_2CHPhCOPh$, followed by acid-catalyzed dehydration.[2a] Ia: by DCl–CD_3COOD cleavage of 1-benzoyl-1,2,2-triphenylcyclopropane; nmr (CCl_4) aromatic *ca.* τ 2.7, singlet τ 3.32 (20:1).

II: mp 125–127° (*Anal.* Found: C, 89.85; H, 6.12); ν (cm^{-1}, KBr) 1675; $\lambda_{\max}^{\text{abs EtOH}}$ 222 and 248 mμ (ϵ 24,400 and 15,600); nmr ($CDCl_3$) aromatic *ca.* τ 2.7, singlet τ 5.92 (10:1); (in C_6H_6) doublets τ 5.72, 5.93 (J = 6 cps). IIa fraction from column chromatography: nmr ($CDCl_3$) aromatic *ca.* τ 2.5, singlet τ 5.9; (in C_6H_6) singlet 5.93 τ. IIb: by refluxing mixture of CH_3OD, CH_3ONa + II (10 days); *ca.* 80% α-D by nmr (C_6H_6): diminished doublet τ 5.93, singlet τ 5.70.

IV: mp 141.5–142.5° (*Anal.* Found: C, 90.2; H, 6.3); $\lambda_{\max}^{\text{abs EtOH}}$ 254 mμ (ϵ 17,000); ν (cm^{-1}, KBr) 3515; nmr ($CDCl_3$) aromatic *ca.* τ 2.9, doublets τ 3.45, 5.5 (J = 11.0 cps), singlet τ 7.5 (vanishing with D_2O) (25:1:1:1).

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Received January 10, 1966

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[6] (a) *Cf.* J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962). (b) The presumably labile *cis* isomer was not isolated and has not yet been made.

[7] C^{14} counts assume III to be oxidized to one hot and one cold molecule of benzoic acid and were semiquantitative because of paucity of materials. The low values might conceivably be due to competing phenyl group migration in II → III (unlikely) or 2 to 3 phenyl migration in I* → III* (inconsistent with oxidation of III* to cold benzoic acid). Further experiments are needed to determine the reality and extent of such migrations.

[8] It might be predicted from the above that irradiation of γ-bromodypnone would first cause photoenolization and ketonization to the isomeric (unknown) β,γ-unsaturated ketone [*cf.* O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963)] and photocyclization of this to a bromo analog of VI, with bromine serving as a leaving group (*e.g.*, collapse by dehydrobromination of a 3-bromo derivative of type VI to 2,4-diphenylfuran). The experiment was performed and indeed gave this furan [however, the same result can be obtained by acid catalysis; *cf.* R. E. Lutz, L. T. Slade, and P. A. Zoretic, *J. Org. Chem.*, **28**, 1358 (1963)]. Furthermore, unsaturated ketone I reacted with NBS, with 4 to 3 phenyl migration, giving tetraphenylfuran. Investigations in this field are in progress.

[9] (a) Shell Co. Fellowship, 1965; (b) Eastman Kodak Co. Fellowship, 1965; (c) this work was supported in part also by a National Science Foundation Research Grant (G-25029).