which ultimately produces 13% ring-deuterated fulvenallene. Most interestingly, pyrolysis of **4b** at moderate temperature (480°) and low pressure (0.02 Torr) gave **9b** with a decreased amount (77%) of deuterium in the methylene position.[12] This decrease in selectivity between the two pathways for rearrangement provides additional evidence[5] that under such conditions **6** is formed initially with vibrational energy greatly in excess of both its own ground state and the threshold for rearrangement to **9**.

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(12) (a) Nmr analysis of recovered **6b** from a pyrolysis of **6b** at 590° showed no detectable hydrogen at C_6 and C_7, under conditions where >5% would have been readily observed; (b) integration of the nmr spectra of **9b** before and after thermolysis at 590° showed no significant decrease in deuterium content in the terminal methylene position.

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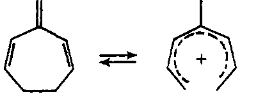
Photochemistry of 2,6-Cycloheptadienones in Strong Acid. A Protonated Version of Cycloheptadienone–Oxyheptatrienyl Transformation

Sir:

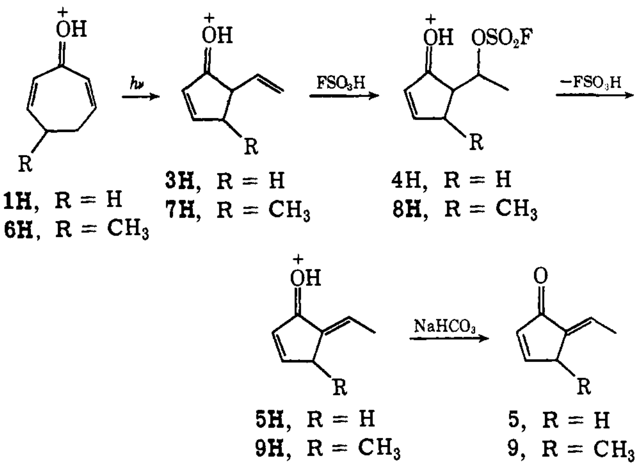
The interconversion of the cyclic dienone **1** and the open-chain dipolar ion **2** (eq 1), although without precedent, has been of theoretical interest in connection with the cyclopropanone–oxyallyl relationship.[1] This paper describes a new photochemical rearrangement of **1** in strong acid medium, which involves the protonated version of eq 1 as the key step.

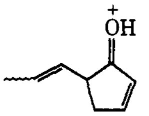


1 **2** (1)

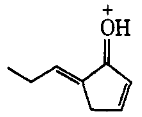
Extraction of **1** with FSO_3H from CCl_4 solution gave the protonated species **1H**,[2,3] which was stable below room temperature and remained unchanged after standing in the dark for extended periods. When the solution, placed in a Pyrex nmr tube, was irradiated at −78° with a 200-W high-pressure Hg arc, a clean rearrangement took place, and after 24-hr irradiation **3H** was produced as the sole species observable by nmr (Scheme I).[4] Warming the photolysate slowly to room temperature led to the formation of the more stable isomer **5H** in addition to some polymeric substances. The isomerization proved to occur, at least mainly, *via* the fluorosulfonate **4H**, which showed characteristic nmr signals at δ 2.10 (d, J = 6.5 Hz, CH_3) and 5.8–6.2 (m, $CHOSO_2F$). Careful neutralization of the acid solution containing **3H** or **5H** with $NaHCO_3$–ether at 0° gave the unprotonated ketone **5**, which upon dissolving in FSO_3H regenerated **5H**.[5] Catalytic hydrogenation of **5** over 10% Pd/C (in C_2H_5OH, 25°) gave 2-ethylcyclopentanone. Photolysis of the methylated derivative **6H** under comparable conditions led to the selective formation of **7H**. Subsequent thermal isomerization afforded **9H**.[6] No signs of the production of the isomer **10H** or **11H** were observed.

Scheme I





10H



11H

The course of the photoreaction was unaffected by the wavelength of incident light (Pyrex (>280 nm), aqueous $CuSO_4$ (>350 nm), or I_2 in CCl_4 (>370 nm) as filter) or reaction temperature (−78 to 0° range).[7]

The photoinduced rearrangement could be rationalized by a stepwise mechanism involving as the key step a protonated version of eq 1 (Scheme II). The protonated dienone **12H** is considered to be in resonance

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(1) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(2) The symbol **H** in the formula number refers to an oxygen-protonated ketone throughout this paper.

(3) Chemical shifts of nmr are expressed in parts per million downfield from TMS as external standard in FSO_3H and internal standard in CCl_4: nmr of **1H** δ 3.17 (br s, CH_2), 7.05 (d, J = 12 Hz, COC*H*=CH), and 8.17 (br d, COCH=C*H*); uv (FSO_3H) 267 (log ϵ 3.95) and 335 sh nm (3.55).

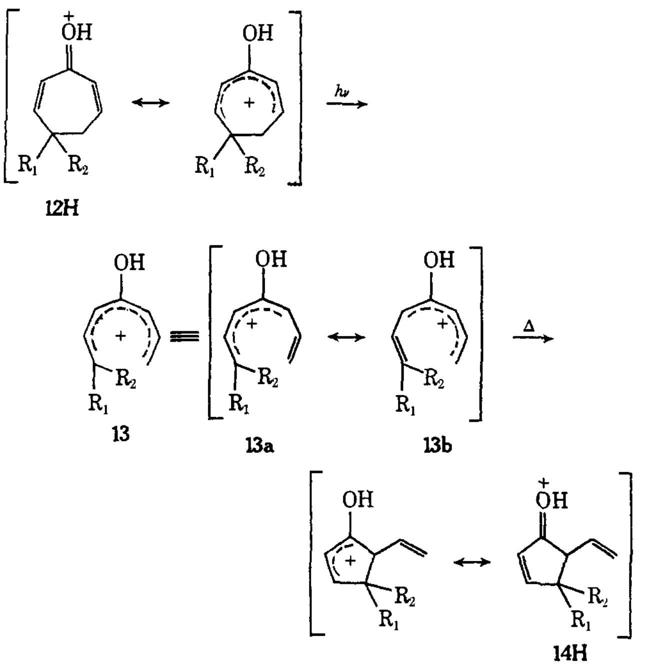
(4) Nmr δ 3.5–4.7 (m, allylic CH_2 and CH), 5.90 (br s, vinyl), 7.30 (br d, COC*H*=CH), and 9.50 (br d, COCH=C*H*).

(5) Nmr of **5H** δ 2.61 (d, J = 7.5 Hz, CH_3), 4.00 (br s, CH_2), 7.29 (d of t, J = 5.2 and 2.1 Hz, COC*H*=CH), 8.22 (q, =C*H*CH_3), and 8.98 (m, COCH=C*H*). Ketone **5**: ir (CCl_4) 1700 (C=O) and 1660 cm^{-1} (C=C); uv (C_2H_5OH) 244 nm (log ϵ 3.93); mass (70 eV) *m/e* 108 (M^+); nmr (CCl_4) δ 1.86 (d, J = 7.5 Hz, CH_3), 3.15 (br s, CH_2), 6.25 (d of t, J = 6 and 2 Hz, COC*H*=CH), 6.50 (q, J = 7.5 Hz, =C*H*CH_3), and 7.45 (m, COCH=C*H*). The stereochemical assignment of the =$CHCH_3$ moiety rested on the chemical shift of the signal due to the olefinic proton: the trans olefinic proton was reported to give a signal at δ ~6.6 and the cis olefinic proton at δ ~5.7 [J. E. Dubois and M. Dubois, *C. R. Acad. Sci., Ser. C*, **256**, 715 (1963); see also, R. A. J. Smith and T. A. Spencer, *J. Org. Chem.*, **35**, 3220 (1970)].

(6) Nmr of **6H** δ 1.57 (d, J = 7.5 Hz, CH_3), 2.9–3.6 (m, allylic CH_2 and CH), 6.8–7.2 (m, COC*H*=CH), and 7.8–8.4 (m, COCH=C*H*). Nmr of **7H** (stereochemistry unknown) δ 1.50 (br d, CH_3), 3.7–4.5 (m, allylic CH), 5.82 (br s, vinyl), 7.20 (br d, COC*H*=CH), and 9.30 (br d, COCH=C*H*). Nmr of **9H** δ 1.73 (d, J = 7.5 Hz, >CHC*H*$_3$), 2.61 (d, J = 7.5 Hz, =CHC*H*$_3$), 4.25 (br q, >C*H*CH_3), 7.21 (d of d, J = 5.2 and 1.5 Hz, COC*H*=CH), 8.19 (q, J = 7.5 Hz, =C*H*CH_3), 8.92 (br d, COCH=C*H*). Ketone **9** showed the following spectral characteristics: ir (CCl_4) 1703 (C=O) and 1655 cm^{-1} (C=C); uv (C_2H_5OH) 244 nm (log ϵ 3.92); mass (70 eV) *m/e* 122 (M^+); nmr (CCl_4) δ 1.29 (d, J = 7.5 Hz, >CHC*H*$_3$), 1.90 (d, J = 7.5 Hz, =CHC*H*$_3$), 3.2–3.7 (m, >C*H*CH_3), 6.17 (d of d, J = 6.0 and 1.5 Hz, COC*H*=CH), 6.48 (q, J = 7.5 Hz, =C*H*CH_3), and 7.33 (d of d, J = 6.0 and 2.5 Hz, COCH=C*H*).

(7) The mode of the present reaction exhibits a striking contrast to those of the previously discovered photoreactions of **1** [H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 3635 (1968)].

Scheme II



with the corresponding hydroxypentadienyl cation having a 4π-electron system.[8] The cationic species is thermally stable since the symmetry-allowed ring closure in a conrotatory fashion[8] is precluded by the existence of the $CR_1R_2CH_2$ bridge. Upon irradiation, it undergoes conrotatory ring opening to produce the reactive cation **13**, which, in turn as vinylpentadienyl cation, gives rise *via* thermal, conrotatory cyclization to the protonated five-membered ketone of type **14H**.[9] Regioselectivity of the rearrangement of unsymmetrical substrates would be controlled by the relative significance of resonance canonical forms of the cation **13**. Introduction of the methyl group at the terminal position should perturb the resonance hybrid **13a** ↔ **13b** ($R_1 = CH_3$ and $R_2 = H$, or $R_1 = H$ and $R_2 = CH_3$) so as to increase the contribution of **13a** leading to **14H**, as is consistent with the finding (**6H** → **7H**). Attempts to detect the cations of type **13** with spectroscopic aids at −78° have not yet met with success.[10]

The rearrangement of the protonated seven-membered dienones might *a priori* be interpreted as a concerted [1,3] sigmatropic reaction from an excited state having a conformation distorted considerably from the planar form. The direct process, however, could not account for the observed regioselectivity of the reaction.

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[8] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 58.

[9] For the facile conversion of pentadienyl cation to cyclopentenyl cation, see P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6404 (1969). The related cyclization of heptatrienyl cation to vinylcyclopentenyl cation is known as well [T. S. Sorensen, *ibid.*, 87, 5075 (1965)].

[10] Stability of hydroxy polyenylic cations is highly influenced by the position of the OH group, as might be rationalized in terms of *formal charge* calculated by the Pople method (M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 183). Protonated forms of conjugated ketones, which can be viewed as cations having OH function at the odd-numbered carbon atom (cationic center), are generally stable. In contrast, no confirmatory evidence for stable cations bearing an OH group at an even-numbered carbon atom of the conjugated system has been presented, though their intermediary existence has very frequently been postulated (for example, see ref 11). Only the nmr of cyclopropanone in FSO_3H–SO_2 at −80° was tentatively interpreted in terms of a mixture of protonated cyclopropanone and 2-hydroxyallyl cation.[12]

[11] B. Parrington and R. F. Childs, *Chem. Commun.*, 1581 (1970); N. Filipescu and J. W. Pavlik, *J. Amer. Chem. Soc.*, **92**, 6062 (1970); K. E. Hine and R. F. Childs, *ibid.*, **93**, 2323 (1971).

[12] G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).

Organocopper Chemistry. Halo-, Cyano-, and Carbonyl-Substituted Ketones from the Corresponding Acyl Chlorides and Organocopper Reagents

Sir:

Organic chemists are continually seeking new reagents for specific and mild formation of carbon–carbon bonds. Organocopper reagents are now becoming widely used in conjugate addition reactions with α,β-unsaturated carbonyl substrates[1] and in coupling reactions with organic halides.[2] We have recently reported formation of methyl and *n*-alkyl ketones from carboxylic acid chlorides and lithium diorganocuprate(I) reagents,[3] and now we describe a significant extension of this ketone synthesis to acid chlorides substituted by iodo, cyano, acyl, and carbalkoxy groups (eq 1). The

$$R'COCl + R_2CuLi \xrightarrow[-78^\circ]{Et_2O} R'COR \qquad (1)$$

relative and absolute reactivities of these functional groups toward organocopper reagents are established, thus defining conditions for other synthetic applications of these versatile reagents.

Summarized in Table I are the transformations which have been achieved using as representative *n*-alkylcopper reagents lithium dimethylcuprate(I) and lithium di-*n*-butylcuprate(I) in diethyl ether at −78° for 15 min. A typical procedure is illustrated by reaction of 6-oxodecanoyl chloride with lithium di-*n*-butylcuprate(I). Into a dry 50-ml two-necked round-bottomed flask equipped with a rubber septum was placed a magnetic stirring bar and cuprous iodide[4] (571 mg, 3.00

Table I. Reaction of Lithium Diorganocuprates(I), R_2CuLi, with Carboxylic Acid Chlorides in Diethyl Ether at −78° (Eq 1)

Acid chloride	Product	R, % yield[a] CH_3	 n-C_4H_9
$CN(CH_2)_{10}COCl$	$CN(CH_2)_{10}COR$	80	>95
n-$C_4H_9CO(CH_2)_4COCl$	n-$C_4H_9CO(CH_2)_4COR$	95	83
$CH_3O_2CCH_2CH_2COCl$	$CH_3O_2CCH_2CH_2COR$	<20	85
n-$C_4H_9O_2C(CH_2)_4COCl$,	n-$C_4H_9O_2C(CH_2)_4COR$	83[b]	93[b]
$ClCO(CH_2)_4COCl$	$RCO(CH_2)_4COR$	92	90
$I(CH_2)_{10}COCl$	$I(CH_2)_{10}COR$	91	93
p-IC_6H_4COCl	p-IC_6H_4COR	98	85
C_6H_5COF	C_6H_5COR	72	87

[a] Yield of isolated product. [b] Yield determined by quantitative vpc analysis.

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[1] G. H. Posner, *Org. React.*, **19**, 1 (1972).

[2] (a) G. H. Posner, manuscript in preparation; (b) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969), and references cited therein.

[3] G. H. Posner and C. E. Whitten, *Tetrahedron Lett.*, 4647 (1970).

[4] "Cuprous iodide purified" was purchased from Fisher Chemical Co. and was used without further purification.