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Addition Reactions of Triphenylgermyllithium with Carboxylic Acid Chlorides

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The reaction of triphenylgermyllithium with carboxylic acid chlorides yields as principal products either α-germyl ketones or bis(triphenylgermyl)carbinols, depending upon reactants and conditions. The influence of substituents in the yellow *para*-substituted benzoyltriphenylgermanes on the energy of the carbonyl n–π^* transition is discussed.

Introduction

The synthesis of compounds containing germanium contiguous to an organic functional group is usually difficult owing to the tendency of intermediates, such as organolithium and Grignard reagents, to react with the organic functional group. One goal of this research was the preparation of a series of α-triphenylgermyl ketones from the reaction of triphenylgermyllithium with carboxylic acid chlorides. Another goal involved the observation of the effects caused by various substituents on the triphenylgermyl keto group.

Unusual reactivities have been observed[2-6] for several organosilicon compounds containing silicon bonded to an organic functional group, and the term "α silicon effect" was introduced.[2] These studies showed that a germanium atom can also impart unusual reactivity to an organic functional group.

From the reaction of triphenylsilyllithium (or triphenylgermyllithium) with methyl triphenylsilanecarboxylate (or methyl triphenylgermanecarboxylate) no bistriphenylsilyl ketone (or bistriphenylgermyl ketone) was isolated; carbon monoxide evolved and hexaphenyldisilane (or hexaphenyldigermane) was formed in high yield.[7]

Benzoyltriphenylsilane, the first example of an α-silyl ketone, was prepared from the reaction of triphenylbenzylsilane and *n*-bromosuccinimide and subsequent hydrolysis of the resulting dibromo derivative.[8] Subsequently, other benzoylsilanes and benzoyltriphenylgermane were prepared.[9,10] Benzoyltriphenylsilane was also obtained from benzoyl chloride and triphenylsilylpotassium, but the yield was only 4%.[8]

The reaction of triphenylsilyllithium and acetyl chloride gives triphenyl(1-phenylsiloxyethyl)silane, triphenylsilane, 1,1-bis(triphenylsilyl)-1-ethanol, and low yields (8.3%) of acetyltriphenylsilane.[11] No propionyl-

triphenylsilane was obtained from the reaction of propionyl chloride with triphenylsilyllithium.[12] When phenylacetyl chloride was allowed to react with triphenylsilyllithium, triphenylsilane was formed owing to abstraction of the acidic hydrogen.[12] Hexaphenylditin and the dibenzoate of *cis*-1,2-stilbenediol are formed during the reduction of benzoyl chloride by triphenyltinsodium.[13]

Experimental

All melting points reported herein are uncorrected. All manipulations involving oxygen- and moisture-sensitive substances were carried out in an atmosphere of dry oxygen-free nitrogen. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Infrared spectra of Nujol mulls of the compounds were taken on a Beckman IR-9 recording spectrophotometer. Ultraviolet and visible spectra were taken in heptane and in ethyl ether solution on a Cary Model 14 recording spectrophotometer. The resolution was appreciably better in heptane than in ethyl ether.

n-Butyllithium was purchased as a 15% solution in hexane from the Foote Mineral Co. Tetrahydrofuran, purchased from Distillation Products, Inc., was purified by refluxing over lithium aluminum hydride and distilled immediately prior to use.

For the preparation of triphenylgermane, the procedure in *Inorganic Syntheses*[14] was modified slightly. Tetraphenylgermane, prepared in the usual manner from germanium tetrachloride, was dissolved in carbon tetrachloride, bromine was added, and the reaction mixture was refluxed for 4 hr. The solvent was stripped and the resulting solid was washed with absolute methanol and recrystallized from glacial acetic acid. For the conversion of triphenylbromogermane to triphenylgermane, the ether solution from the reduction with lithium aluminum hydride was carefully hydrolyzed with dilute hydrochloric acid, separated, and dried over anhydrous sodium sulfate. The ether was then stripped and methanol was added. Upon cooling, triphenylgermane crystallized. The over-all yield of the three steps was about 50%.

For a typical preparation of triphenylgermyllithium, 5 g. (0.016 mole) of triphenylgermane was dissolved in 150 ml. of tetrahydrofuran, the solution was cooled to −23° with a Dry Ice–carbon tetrachloride bath, and 10.4 ml. of *n*-butyllithium solution (0.016 mole) was added slowly with rapid stirring. The resulting pale green solution was stirred for 0.5 hr.

Benzoyl Chloride and Triphenylgermyllithium.—The following preparation of benzoyltriphenylgermane is typical of all preparations carried out in this study. Minor variations in order of addition of reagents and in temperature are noted in the titles.

(1) Alfred P. Sloan Research Fellow.
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(3) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *ibid.*, **76**, 1613 (1954).
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(9) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).
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(13) D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 618 (1961).
(14) D. M. Harris, W. H. Nebergall, and O. H. Johnson, *Inorg. Syn.*, **5**, 70 76 (1957).

Also, some other minor variations in procedure are recorded elsewhere.[15]

Addition of Triphenylgermyllithium to Benzoyl Chloride at −23°.—To a mechanically stirred 500-ml. three-necked flask was added a solution of 4.6 g. (0.032 mole) of benzoyl chloride (freshly distilled, b.p. 190–191°) in 150 ml. of tetrahydrofuran. To a dropping funnel connected to one neck of the flask was added a solution of 0.016 mole of triphenylgermyllithium in tetrahydrofuran. The flask was cooled to −23° with a Dry Ice–carbon tetrachloride bath. The dropping funnel was cooled with crushed Dry Ice held by a metal jacket. The triphenylgermyllithium solution was added to the benzoyl chloride solution dropwise, rapid stirring of the benzoyl chloride solution being maintained throughout the addition. The resulting yellow solution was stirred an additional 0.5 hr. at −23° after addition was complete and then allowed to warm slowly to room temperature. After being stirred for 30 min. at room temperature the solution was hydrolyzed with dilute hydrochloric acid. Ethyl ether was added and the aqueous layer was separated and discarded. The ether layer was washed again with dilute hydrochloric acid and then dried over anhydrous sodium sulfate. After removal of sodium sulfate by filtration and of the ether by stripping, hexane was added. A yellow solid separated (*ca.* 0.1 g.) and the solution was filtered. The filtrate was chromatographed on acid-washed alumina with 250-ml. portions of hexane, carbon tetrachloride, benzene, chloroform, and acetone, successively.

From the hexane eluent, 0.1 g. of triphenylgermane was recovered.

The carbon tetrachloride eluent was stripped and 25 ml. of petroleum ether (b.p. 33–60°) was added. A bright yellow solid, benzoyltriphenylgermane, precipitated from the cooled solution and was recrystallized from petroleum ether; m.p. 103–106°; yield 3.0 g. (45%).

Anal. Calcd. for $C_{25}H_{20}GeO$: C, 73.4; H, 4.9. Found: C, 73.6; H, 5.1.

From a similar treatment of the benzene eluent, a yellow solid (0.4 g., 6%) was obtained and shown by mixture melting point to be identical with the product from the carbon tetrachloride eluent.

The chloroform eluent was stripped and 25 ml. of petroleum ether was added. A white solid, hexaphenyldigermoxane, precipitated and was recrystallized from petroleum ether; m.p. 182–184°; yield 0.2 g. (4%).

Anal. Calcd. for $C_{36}H_{30}Ge_2O$: C, 69.3; H, 4.9. Found: C, 69.3; H, 4.9.

The acetone eluent, treated as above, produced 0.2 g. (10%) of benzoic acid; m.p. 117–121°.

Anal. Calcd. for $C_7H_6O_2$: C, 68.8; H, 5.0. Found: C, 69.0; H, 5.0.

Addition of Benzoyl Chloride to Triphenylgermyllithium at −23°.—Benzoyltriphenylgermane was the only product isolated from the reaction; m.p. 100–102°; yield 48%.

Anal. Calcd. for $C_{25}H_{20}GeO$: C, 73.4; H, 4.9. Found: C, 73.1; H, 5.1.

Addition of Triphenylgermyllithium to Benzoyl Chloride at −78°.—Benzoyltriphenylgermane was isolated and identified by mixture melting point with the material prepared above; m.p. 100–102°; yield 80%.

Addition of Benzoyl Chloride to Triphenylgermyllithium at 25°. —A very light yellow solid, bis(triphenylgermyl)phenylcarbinol, was isolated and recrystallized from heptane; m.p. 183–185°; yield 49%.

Anal. Calcd. for $C_{43}H_{36}Ge_2O$: C, 72.3; H, 5.1. Found: C, 72.1; H, 5.2.

No other products were isolated.

Addition of Triphenylgermyllithium to Benzoyltriphenylgermane at 25°.—The reaction of equimolar portions of triphenylgermyllithium and benzoyltriphenylgermane resulted in the formation of 1,1-bis(triphenylgermyl)phenylcarbinol identified by mixture melting point; m.p. 183–186°; yield 57%.

(15) D. A. Nicholson, Thesis, Northwestern University, 1965.

Acetyl Chloride and Triphenylgermyllithium. Addition of Triphenylgermyllithium to Acetyl Chloride at −23°.—Triphenylgermyllithium reacted with a twofold excess of acetyl chloride (freshly distilled, b.p. 51–52°) to produce 1,1-bis(triphenylgermyl)-1-ethanol, which after repeated recrystallizations from benzene–hexane and heptane melted in the range 208–210°; yield 54%. The melting point of the material dropped to around 200° after aging for a few days.

Anal. Calcd. for $C_{38}H_{34}Ge_2O$: C, 70.0; H, 5.3. Found: C, 70.4; H, 5.4.

No other products were isolated.

Addition of Acetyl Chloride to Triphenylgermyllithium at −23°.—Reverse addition of the reagents led to an 85% yield of 1,1-bis(triphenylgermyl)-1-ethanol, identified by mixture melting point; m.p. 200–202°.

Anal. Found: C, 70.4; H, 5.3.

Addition of Triphenylgermyllithium to Acetyl Chloride at −78° —Only 1,1-bis(triphenylgermyl)-1-ethanol was isolated; yield 67%.

Addition of Triphenylgermyllithium to Propionyl Chloride at −78°.—From equimolar amounts of the reactants, a white solid, 1,1-bis(triphenylgermyl)-1-propanol, was isolated and recrystallized twice from hexane; m.p. 178–181°; yield 37%.

Anal. Calcd. for $C_{39}H_{36}Ge_2O$: C, 70.3; H, 5.4. Found: C, 70.3; H, 5.4.

***p*-Methoxybenzoyl Chloride and Triphenylgermyllithium.**—Triphenylgermyllithium was added to *p*-methoxybenzoyl chloride at −78°. The yellow product, *p*-methoxybenzoyltriphenylgermane, was recrystallized from hexane–benzene and from heptane; m.p. 136–138.5°; yield 84%.

Anal. Calcd. for $C_{26}H_{22}GeO_2$: C, 71.1; H, 5.1. Found: C, 70.9; H, 5.0.

Attempted Addition of Triphenylgermyllithium to *p*-Methoxybenzoyltriphenylgermane at 25°.—No reaction occurred when these reagents were combined in the usual manner. *p*-Methoxybenzoyltriphenylgermane (86%) was recovered; m.p. 136–139°.

***p*-Fluorobenzoyl Chloride and Triphenylgermyllithium.**—Triphenylgermyllithium was added to an equimolar quantity of *p*-fluorobenzoyl chloride at −78° and two products were isolated. A pentane-insoluble white solid, bis(triphenylgermyl)-*p*-fluorophenylcarbinol, was recrystallized from hexane–benzene; m.p. 187–190°; yield 60%.

Anal. Calcd. for $C_{43}H_{35}Ge_2OF$: C, 70.6; H, 4.8. Found: C, 70.9; H, 5.0.

The second product, yellow *p*-fluorobenzoyltriphenylgermane, was recrystallized from pentane and from 95% ethanol; m.p. 118–120°; yield 22%.

Anal. Calcd. for $C_{25}H_{19}GeOF$: C, 70.3; H, 4.5. Found: C, 70.6; H, 4.6.

Addition of Triphenylgermyllithium to *p*-Trifluoromethylbenzoyl Chloride at −78° in Ethyl Ether.—The previous procedure led to a bright yellow solid, *p*-trifluoromethylbenzoyltriphenylgermane; m.p. 116–118°; yield 44%.

Anal. Calcd. for $C_{26}H_{19}GeOF_3$: C, 65.5; H, 4.0. Found: C, 65.5; H, 4.2.

Phosgene and Triphenylgermyllithium.—Triphenylgermyllithium (0.016 mole) in tetrahydrofuran was added to a solution of phosgene (4.0 g., 0.0405 mole) in benzene–tetrahydrofuran at −78°. Cloudiness developed in the solution immediately. The solution was hydrolyzed as soon as addition was complete. Filtration of this solution yielded 3.9 g. (78%) of hexaphenyldigermane; m.p. 343–346°.

Anal. Calcd. for $C_{36}H_{30}Ge_2$: C, 71.1; H, 5.0. Found: C, 70.9; H, 4.8.

Results

The reaction of triphenylgermyllithium with a series of carboxylic acid chlorides yields α-triphenylgermyl ketones or bis(triphenylgermyl)carbinols, depending on reactants and reaction conditions. At −23° addition of triphenylgermyllithium to benzoyl chloride gives

TABLE I

KETONES FROM THE REACTIONS OF TRIPHENYLGERMYLLITHIUM
WITH SUBSTITUTED BENZOYL CHLORIDES AND CORRESPONDING
VISIBLE SPECTRA DATA

	Diethyl ether Maxima, mμ	Heptane Maxima, mμ	ϵ
$(C_6H_5)_3Ge-\overset{\overset{O}{\|\|}}{C}-C_6H_5$	439 sh^a	440 sh^a	123
	415.7	417.5	210
	396 sh	401.2	173
	…	…	
$(C_6H_5)_3Ge-\overset{\overset{O}{\|\|}}{C}-C_6H_4OCH_3\text{-}p$	426 sh	424	189
	404.3	406.0	280
	386 sh	389.5	218
	…	…	
$(C_6H_5)_3Ge-\overset{\overset{O}{\|\|}}{C}-C_6H_4F\text{-}p$	435 sh	436 sh	141
	411.2	412.6	243
	392 sh	395.7	196
		375 sh	101
$(C_6H_5)_3Ge-\overset{\overset{O}{\|\|}}{C}-C_6H_4CF_3\text{-}p$	…	458 sh	91
	428.2	429.5	178
	409 sh	416	162
	…	…	

^{a} sh, shoulder.

TABLE II

INFRARED ASSIGNMENTS

Compound	C=O stretch, cm.$^{-1}$	O—H stretch, cm.$^{-1}$	C$_6$H$_5$—Ge stretch, cm.$^{-1}$
$(C_6H_5)_3GeC(O)C_6H_5$	1625	…	1085
			1429
$(C_6H_5)_3GeC(O)C_6H_4OCH_3\text{-}p$	1628	…	1090
			1430
$(C_6H_5)_3GeC(OH)(CH_3)Ge(C_6H_5)_3$	…	3520	1081
			1430
$p\text{-}FC_6H_4C(O)Ge(C_6H_5)_3$	1628	…	1090
			1430
$p\text{-}F_3CC_6H_4C(O)Ge(C_6H_5)_3$	1637	…	1090
			1430
$(C_6H_5)_3GeC(OH)(C_6H_4F\text{-}p)Ge(C_6H_5)_3$	…	3480	1088
			1430
$(C_6H_5)_3GeC(OH)(C_6H_5)Ge(C_6H_5)_3$	…	3480	1089
			1430

benzoyltriphenylgermane in 51% yield. With the reverse order of addition at $-23°$, the yield of benzoyltriphenylgermane only drops to 48%. At $-78°$ the yield of benzoyltriphenylgermane increases to 80%; and at 25° with a 2:1 ratio of triphenylgermyllithium to benzoyl chloride, bis(triphenylgermyl)phenylcarbinol is obtained in 49% yield. Also, the reaction of benzoyltriphenylgermane and triphenylgermyllithium gives bis(triphenylgermyl)phenylcarbinol at room temperature.

The products from the combination of triphenylgermyllithium with some *para*-substituted benzoyl chlorides are indicated in Table I.

No ketones were isolated from the reactions of aliphatic acid chlorides with triphenylgermyllithium.
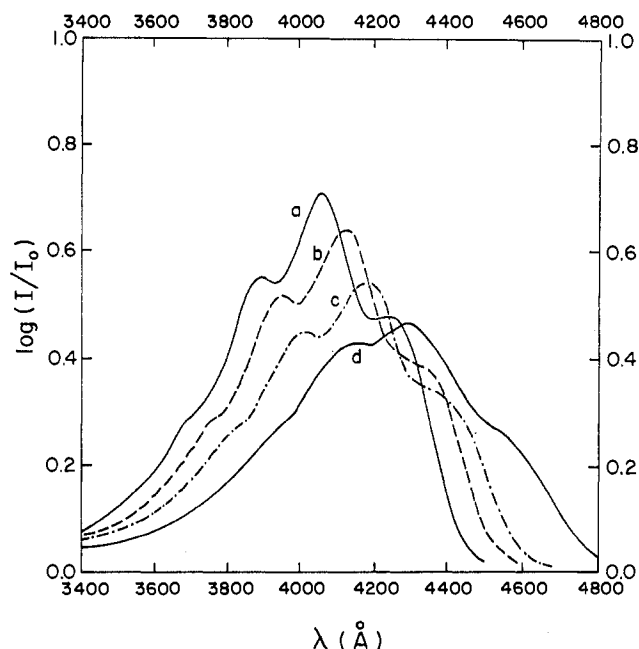

Figure 1.—Visible spectra in heptane of (a) p-methoxybenzoyltriphenylgermane $(2.50 \times 10^{-3} M)$; (b) p-fluorobenzoyltriphenylgermane $(2.67 \times 10^{-3} M)$; (c) benzoyltriphenylgermane $(2.56 \times 10^{-3} M)$; (d) p-trifluoromethylbenzoyltriphenylgermane $(2.60 \times 10^{-3} M)$.
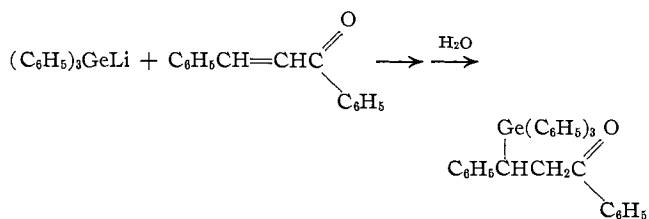
From the reactions involving acetyl chloride and propionyl chloride, 1,1-bis(triphenylgermyl)-1-ethanol and 1,1-bis(triphenylgermyl)-1-propanol were the principal products.

The characteristic infrared absorption frequencies for the C=O stretch, the O—H stretch, and the C$_6$H$_5$—Ge stretch are presented in Table II. The absorption at 1090 cm.$^{-1}$ is diagnostic for phenyl attached to germanium.

The absorption maxima and molar absorptivities of the ketones prepared in this study are listed in Table I. The spectra taken with heptane as the solvent are presented in Figure 1.

Discussion

The substitution of the triphenylgermyl group at the aromatic acid chloride becomes more favorable than the addition across the carbon–oxygen double bond as the temperature is decreased. However, the above experiments do not establish if the former reaction proceeds by simple substitution or by the formation of an intermediate such as $Li^+[(C_6H_5)_3GeC(-O)Cl(R)]^-$ and then elimination of lithium chloride. The addition of triphenylgermyllithium to a carbon–carbon double bond is more favorable than addition to a carbonyl group in the reaction[16]

$$(C_6H_5)_3GeLi + C_6H_5CH=CHC\overset{\overset{O}{/\!\!/}}{\underset{C_6H_5}{\diagdown}} \xrightarrow{\ \ } \xrightarrow{H_2O}$$

$$\underset{C_6H_5CHCH_2C}{\overset{Ge(C_6H_5)_3}{|}}\overset{O}{\overset{/\!\!/}{\diagdown}}_{C_6H_5}$$

(16) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **79**, 342 (1957).

The preparation of α-germyl ketones and of bis(triphenylgermyl)carbinols from triphenylgermyllithium and carboxylic acid chlorides is much more feasible than similar reactions involving analogous triphenyl derivatives of silicon and tin.

Visible Spectra.—The most interesting property of Brook's original α-silyl ketone, benzoyltriphenylsilane, is its yellow color.[8] The color is due to the n–π^* transition of the carbonyl group occurring in the visible region. Further studies[9,10] confirmed that several benzoylsilane derivatives absorb in this region of the spectrum. The substitution of different R groups in $C_6H_5C(=O)SiR_3$ only alters slightly the position of the n–π^* transition.

The shift of the carbonyl n–π^* transition was first attributed to β-π bonding between the group IV-B atom and oxygen.[9] Harnish and West[17] interpreted the observed shift by a model in which the d orbitals of germanium and silicon are perturbing the π^* antibonding orbital of the carbonyl group, with the result that the n–π^* transition is lowered in energy.

The n–π^* transition of the carbonyl group in benzoyltriphenylgermane occurs at 417.5 mμ (in agreement with the value obtained by Brook)[9] in heptane. The carbon analog of benzoyltriphenylgermane, benzoyltriphenylmethane, absorbs at 328.0 mμ.[9] Thus, an unusually large shift of 6535 cm.$^{-1}$ to lower frequency is observed in benzoyltriphenylgermane. The introduction of a methoxy group in the *para* position of benzoyltriphenylgermane causes a shift in the maximum to higher frequency. A *p*-fluoro group gives rise to a slight shift to higher frequency and a *p*-trifluoromethyl group to a shift to lower frequency.

These shifts can be ascribed to the influence of resonance and inductive effects on the separation of electronic energy levels and the corresponding energy required for the n–π^* transition. Fluoro and methoxy groups are classified as $+R$ and $-I$[18] and the trifluoromethyl group is $-R$ and $-I$.[19] The transfer of electron density by the fluoro and methoxy groups to the conjugated systems raises the energy of the π^* orbital of the carbonyl group, thus increasing the separation of the n and π^* levels and shifting the absorption to higher frequency. On the other hand, the ability of the trifluoromethyl group to withdraw electron density lowers the π^* level and shifts the n–π^* transition to lower frequency. The above interpretation of the resonance effect of the *p*-methoxy group is consistent with the fact that no addition of triphenylgermyllithium to *p*-methoxybenzoyltriphenylgermane was observed while an alcohol is formed from triphenylgermyllithium and unsubstituted benzoyltriphenylgermane under comparable conditions.

From a comparison of the visible and ultraviolet spectra of *para*-substituted benzoyltriphenylgermanes, acetophenones,[20] and benzoyltriphenylsilanes,[10] several conclusions can be drawn: The order of substituents for increasing frequency of the n–π^* transition is the same as in the three series.[21] For a given substituent on the phenyl ring bonded to the carbonyl group, the order of increasing frequency for this transition is $-Si(C_6H_5)_3 < -Ge(C_6H_5)_3 \ll -CH_3$. The molar absorptivities for the n–π^* transition of the *para*-substituted benzoyltriphenylgermanes are less than those of analogous silanes and much less than those of analogous acetophenones.

The spectra of ketones with stronger $-R$ or $+R$ groups substituted in the *para* position of the benzoyl group should exhibit greater shifts. The synthesis of many of these compounds would not be expected to be possible by the method previously described because of the tendency of triphenylgermyllithium to react with groups such as $-NO_2$, $-C{\equiv}C$, or $-OH$.

(17) D. E. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963).
(18) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p. 218.
(19) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(20) J. Tanaka, S. Nagakura. and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).
(21) In this research, the n–π^* transition of *p*-methoxyacetophenone in heptane was observed at 352.0, 337.5, 322.2, and 310.9 mμ, a region partially overlapping that of the π–π^* transition.