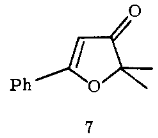
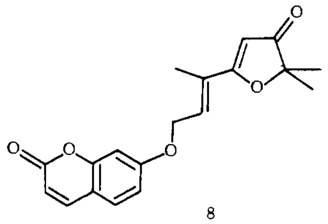
yield from benzaldehyde.[10] Similarly, an antitumor furanone, geiparvarin (**8**),[11] was prepared with stereospecificity from 4-(coumarin-7-yloxy)-2-methyl-2(*E*)-butenal[12] in 52% yield and the spectral data (IR, NMR)[13] as well as the melting point were identical with those of the recorded ones on the natural material.



7



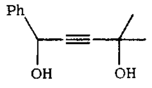
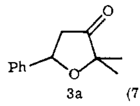
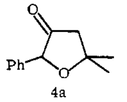
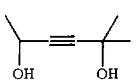
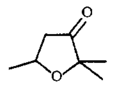
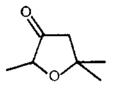
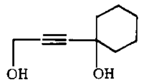
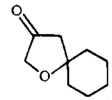
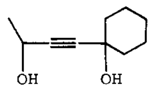
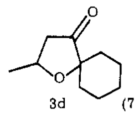
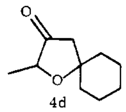
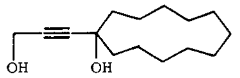
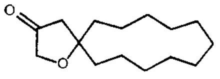
8

For access to the opposite regioisomer **4** of the dihydrofuranones an ethanol solution of the acetylenic diol **1** was stirred with Hg/Nafion-H (0.5 g/mmol of **1**)[4] in the presence of 5 equiv of water at room temperature for 1-7 h. Filtration of the catalyst, concentration, and preparative TLC purification gave **4** as a major product, as listed in Table II. Although the selectivity in **1a**, **1b**, and **1d** (secondary vs. tertiary hydroxyl) was moderate (4:1 to 1:1), the discrimination of the primary hydroxyl group from the tertiary one was excellent as exemplified in the reaction of **1c** and **1h**.

Salient features of the Hg/Nafion-H reagent follow: (1) Workup operation involves only filtration and concentration. (2) The catalyst is recovered easily and reused without loss of Hg(II) ion. For example, 2,5-dimethyl-3-hexyne-2,5-diol was converted into 2,2,5,5-tetramethyl-4,5-dihydro-3(2*H*)-furanone repeatedly (first run, 90% yield, and second run with the recovered reagent, 82%). (3) The reaction proceeds under mild conditions (room temperature) with high selectivity compared with the conventional catalyst HgO (or $HgSO_4$).[2]

Applications of these new methods to the synthesis of other natural products are in progress in our laboratories.

Table II. Hg/Nafion-H Catalyzed Dihydro-3(2*H*)-furanone Synthesis[a]

2-butyne-1,4-diol derivative	dihydro-3(2*H*)-furanone (% yield, product ratio)
 1a	  3a (70, 1:4) 4a
 1b	  3b (80, 1:2) 4b
 1c	 4c only (62)
 1d	  3d (70, 1:1) 4d
 1h	 4h only (68)[b]

[a] A mixture of 1 and water (5 equiv) dissolved in ethanol was stirred at room temperature in the presence of Hg/Nafion-H catalyst (0.5 g/mmol of 1) for 1-7 h. Product was isolated by preparative TLC. [b] A byproduct, 1-cyclododecylidene-3-hydroxy-2-propanone, was formed in 10% yield.

---

(9) (a) Brandt, C. W.; Taylor, W. I.; Thomas, B. R. *J. Chem. Soc.* **1954**, 3245. (b) Parker, W.; Raphael, R. A.; Wilkinson, D. I. *Ibid.* **1958**, 3871. (c) Takeda, A.; Tsuboi, S.; Sakai, T. *Chem. Lett.* **1973**, 425. (d) Baldwin, J. E.; Thomas, R. C.; Kruse, L. I.; Silberman, L. *J. Org. Chem.* **1977**, *42*, 3846. (e) Reffstrup, T.; Boll, P. M. *Acta Chem. Scand., Ser. B* **1977**, *31B*, 727. (f) Smith, A. B., III; Jerris, P. J. *Synth. Commun.* **1978**, *8*, 421. (g) Ito, M.; Ohno, M.; Takano, E.; Oda, Y.; Tsukida, K. *Heterocycles* **1979**, *12*, 505. (h) Rosenkranz, R. E.; Allner, K.; Good, R.; Philipsborn, W. v.; Eugster, C. H. *Helv. Chim. Acta* **1963**, *46*, 1259. (i) Hofmann, A.; Philipsborn, W. v.; Eugster, C. H. *Ibid.* **1965**, *48*, 1322.

(10) The following procedures for bullatenone synthesis are typical. Butyllithium (1.53 M hexane solution, 19.6 mL, 30 mmol) was added to a THF (150 mL) solution of 2-methyl-3-butyn-2-ol (1.26 g, 15 mmol) at -78 °C under an argon atmosphere, and the reaction mixture was stirred for 2 h between -78 and -65 °C. Benzaldehyde (1.06 g, 10.0 mmol) dissolved in THF (4 mL) was added over 10 min at -65 °C, and the resulting solution was stirred for 6 h and allowed to warm to room temperature. Workup followed by column chromatography (silica gel, dichloromethane, then 1:1 hexane-ethyl acetate elution) gave 4-methyl-1-phenyl-2-pentyne-1,4-diol (**1a**) (1.87 g, 98% yield). The adduct **1a** (0.21 g, 1.09 mmol) dissolved in dichloromethane (0.25 mL) was treated with acetic anhydride (0.5 mL) and pyridine (0.05 mL) at room temperature for 2 h. Purification of the concentrated residue by column chromatography (silica gel, hexane-ethyl acetate, from 10:1 to 2:1) gave the corresponding monoacetate (0.25 g, 99% yield). ^1H NMR (CCl_4) δ 1.51 (s, 6 H), 2.03 (s, 3 H), 2.96 (br s, 1 H), 6.41 (s, 1 H), 7.2-7.6 (m, 5 H); IR (neat) 3400, 1740 cm^{-1}. The monoacetate (77 mg, 0.33 mmol) dissolved in benzene (1 mL) was heated at 80 °C in the presence of silver perchlorate (4 mg) for 10 h in the dark under an argon atmosphere. Then the reaction mixture was diluted with dichloromethane (10 mL) and washed with 10% aqueous ammonia (3 mL) and saturated sodium chloride aqueous solution (3 mL). Column chromatography (silica gel, 10:1 hexane-ethyl acetate) of the concentrated crude product gave the enol acetate **2a** (65 mg, 84% yield), bp 122-124 °C (bath temperature) (0.04 torr); IR (neat) 1781, 1698, 1658 cm^{-1}; MS, *m/e* 232 (M^+); ^1H NMR (CCl_4) δ 1.36 (s, 3 H), 1.38 (s, 3 H), 2.17 (s, 3 H), 5.70 (d, J = 1.5 Hz, 1 H), 5.81 (d, J = 1.5 Hz, 1 H), 7.26 (br s, 5 H). The enol acetate (114 mg, 0.49 mmol) was treated with DDQ (161 mg, 0.71 mmol) in benzene (1 mL) at room temperature for 1.8 h. Workup and preparative TLC (20:1 dichloromethane-ethyl acetate) gave bullatenone (**7**) (92 mg, 99% yield). The overall yield from benzaldehyde to bullatenone was 81%.

Treatment of the enol acetate **2a** (33 mg, 0.14 mmol) with sodium methoxide (0.01 mmol) in methanol (1 mL) at room temperature for 0.7 h gave the dihydrofuranone **3a** (24 mg, 90% yield).

(11) (a) Lahey, F. N.; MacLeod, J. K. *Aust. J. Chem.* **1967**, *20*, 1943. (b) Carman, R. M.; Lahey, F. N.; MacLeod, J. K. *Ibid.* **1967**, *20*, 1957. (c) Dreyer, D. L.; Lee, A. *Phytochemistry* **1972**, *11*, 763. (d) Padmawinata, K. *Acta Pharm.* **1973**, *4*, 1; *Chem. Abstr.* **1973**, *79*, 75897n.

(12) The aldehyde was prepared by selenium dioxide oxidation of 7-(3'-methyl-2'-butenyloxy)courmarin: Lassak, E. V.; Southwell, I. A. *Aust. J. Chem.* **1972**, *25*, 2491.

(13) The synthetic material showed more than 97% purity of the *E* isomer as evidenced by ^1H NMR ($CDCl_3$): δ 6.73 (t, J = 6.0 Hz, 1 H, C(7)-H), 4.82 (d, J = 6.0 Hz, 2 H, C(8)=H_2) consistent with the literature values, 6.64 and 4.82 (ref 3a), 6.77 and 4.87 (ref 11b), 6.90 and 4.95 (ref 11c).

Photoexcitation of Nonconjugated, Strained, Saturated Hydrocarbons. Relationship between Ease of Oxidation and Quenching of Naphthalene Fluorescence by Saturated Hydrocarbons

Paul G. Gassman,* Kurt D. Olson,[1] Lee Walter, and
Ryohei Yamaguchi

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received March 30, 1981
Revised Manuscript Received June 12, 1981

Recently, we have examined in detail the oxidation of strained, saturated hydrocarbons.[2] The relative ease with which these hydrocarbons released electrons (0.4-2.1 V vs. SCE[2]) suggested that (a) they might all be effective fluorescence quenchers[3] through

---

(1) University of Minnesota Dissertation Fellow, 1980-1981.

(2) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *Ibid.* **1979**, *101*, 5793. Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

Table I. Fluorescence Quenching of Naphthalene Fluorescence by Highly Strained Polycyclic Molecules

quencher	k_q, L/(mol s^{-1})	$k_q\tau$, L/mol	$E_{1/2}$, V[a]
tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**)	3.20×10^9 [b,c]	307	0.91
1,2,2-trimethylbicyclo[1.1.0]butane (**2**)	1.02×10^8	9.79	1.23
tricyclo[4.1.0.0^{2,7}]heptane (**3**)	2.1×10^7 [c]	2.02	1.50
pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (**4**)	2.2×10^7	2.11	1.73
pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**5**)	1.4×10^7	1.34	1.74
pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**6**)	9.8×10^6	0.94	1.62
pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (**7**)	7.2×10^6	0.69	1.67
bicyclo[2.1.0]pentane (**8**)	2.1×10^6 [c]	0.20	1.91
tricyclo[2.2.1.0^{2,6}]heptane (**9**)	*d*	*d*	2.12

[a] Taken from ref 2. The values cited are measured electrode potentials. It is assumed that the measured electrode potentials are kinetically shifted (due to follow-up reactions) relative to the *reversible* potentials for each hydrocarbon. [b] All fluorescence quenching rates were reproducible to ±5%. [c] See: Taylor, G. N. *Chem. Phys. Lett.* 1971, *10*, 355. [d] Tricyclo[2.2.1.0^{2,6}]heptane gave no observable quenching of naphthalene fluorescence at the concentration used.

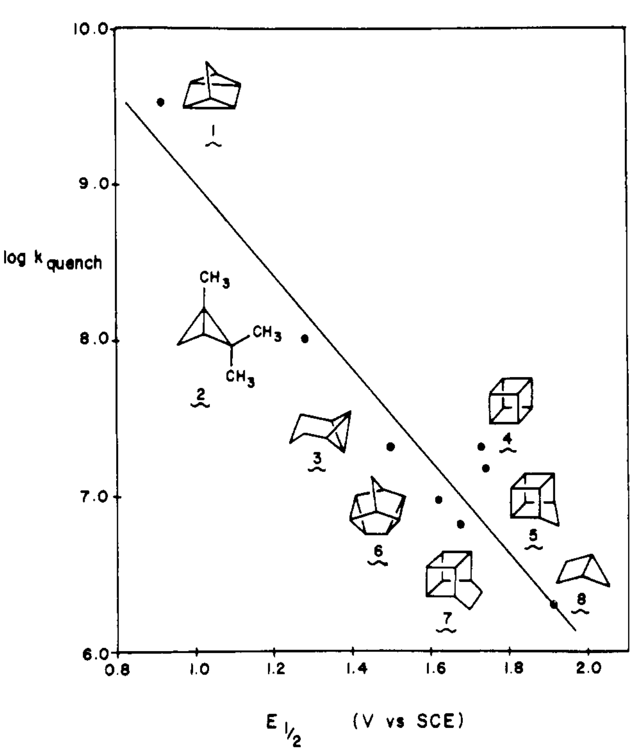


Figure 1. Plot of log k_q for quenching of naphthalene fluorescence vs. oxidation half-wave potentials of a series of highly strained hydrocarbons. Solid line represents the least-squares line.

an electron-transfer process and (b) they might undergo sensitized photochemical reactions. We now wish to report that the rate of fluorescence quenching of naphthalene gives a reasonably good correlation with the oxidative half-wave potentials for a series of highly strained polycyclic hydrocarbons.

Table I lists the Stern–Volmer data (k_q values) and oxidative half-wave potentials ($E_{1/2}$) for a series of highly strained hydrocarbons. The quenching rates were obtained through the use of 9.6×10^{-8} s as the value for the excited singlet lifetime of naphthalene.[4] Excitation was carried out at 280 nm and fluorescence emission was measured at 321 nm by using standard degassed solutions of 5–8 $\times$ 10^{-4} M naphthalene in cyclohexane with varying concentrations of hydrocarbons **1**–**9**. No quenching was observed when **9** was used as the quencher. On the basis of the observed correlation of oxidation half-wave potential with log k_q, it would be predicted that **9** would be at the extreme low end of where quenching might be observed.

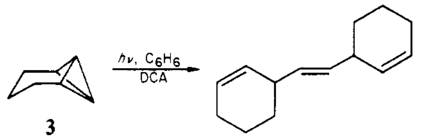
Figure 1 is a plot of log k_q vs. the oxidation half-wave potentials of compounds **1**–**8**. The solid line represents the least-squares fit for the eight compounds. The relationship is represented by

$$\log k_q = -2.92E_{1/2} + 11.95$$

The correlation coefficient for this plot was 0.960.

The correlation observed above suggested that it might be possible to observe photosensitized reactions of various strained saturated hydrocarbons. In order to test this concept, we initially examined the preparative photochemistry of the readily available hydrocarbon **3** with naphthalene in benzene. After several hours only small amounts (2–3%) of **3** had been consumed. Operating on the hypothesis that a reversible electron-transfer process might be involved,[3d,f] 9,10-dicyanoanthracene (DCA) was used as a sensitizer. It was reasoned that 9,10-dicyanoanthracene might be a more efficient sensitizer since its excited-state reduction potential is 2.08 V vs. 1.43 V for naphthalene.[5]

When 60 mL of a benzene solution which had been saturated with DCA (72 mg) and which contained 2.12 g of **3** was irradiated in a Pyrex vessel for 6 h with a 450-W medium-pressure Hanovia lamp, complete reaction of **3** was noted, and a single product was observed by VPC analysis (90% yield). This clear, colorless liquid was distilled to give 1.6 g (75%) of **10**; bp 75–78 °C (0.33 mm).[6]



3

10

^{1}H NMR, ^{13}C NMR, and the mass spectral cracking pattern data were consistent with the assigned structure. In addition, **10** was readily oxidized to *trans*-stilbene by chloranil in benzene at 140 °C.

Mechanistically, **10** is the formal dimer of a carbene, which would be generated if a photochemical retrocarbene addition of **3**[7] were to occur. Since certain carbenoid-type intermediates are effectively trapped by methanol, we explored the photosensitized reaction of **3** in methanol containing 0.1% potassium hydroxide[8]

---

(3) It should be noted that isolated examples of fluorescence quenching by strained hydrocarbons have previously been reported. However, relatively little in the way of product-forming photochemistry has been observed. The major system which has been previously examined is quadricyclane (both bicyclo[2.1.0]pentane and tricyclo[4.1.0.0^{2,7}]heptane have also been evaluated as quenchers). For example, see: (a) Murov, S. L.; Cole, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 2957. (b) Murov, S.; Hammond, G. S. *J. Phys. Chem.* **1968**, *72*, 3797. (c) Solomon, B. S.; Steel, C.; Weller, A. *J. Chem. Soc., Chem. Commun.* **1969**, 927. (d) Taylor, G. N. *Chem. Phys. Lett.* **1971**, *10*, 355. (e) Sasaki, T.; Kanematsu, K.; Ando, I.; Yamashita, O. *J. Am. Chem. Soc.* **1976**, *98*, 2686. (f) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Greenberg, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 681. See also: Gorman, A. A.; Leyland, R. L.; Rodgers, M. A. J.; Smith, P. G. *Tetrahedron Lett.* **1973**, 5085. Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814. Turro, N. J.; Chow, M.-F.; Kanfer, S.; Jacobs, M. *Tetrahedron Lett.* **1981**, 3. Okada, K.; Hisamitsu, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.*, **1980**, 941. Mukai, T.; Satō, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670.

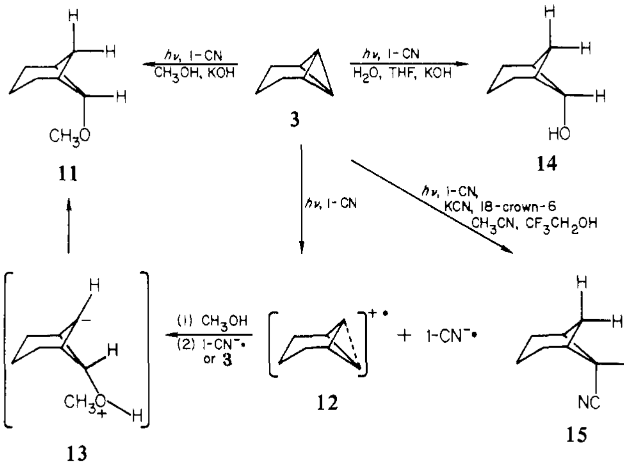
(4) Berlman, I. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed.; Academic Press: New York, 1971; p 73.

(5) Excited-state reduction potentials were calculated by adding the difference between the ground-state and excited-state energies to the $E_{1/2}$ for reduction of the ground state. For leading references, see ref 3f and references contained therein.

(6) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

(7) For leading references to photochemical retrocarbene additions of three-membered rings, see: Griffin, G. W. *Angew Chem., Int. Ed. Engl.* **1971**, *10*, 537. Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 5127.

and 1-cyanonaphthalene as a photosensitizer. Under these conditions, irradiation of **3** with a 450-W, medium-pressure Hanovia lamp through Vycor for 20 h gave a quantitative yield of **11** (by VPC analysis vs. an internal standard). The structure of **11** was established through comparison with an authentic sample synthesized according to the literature procedure.[10]



The facile addition of methanol to **3** under photosensitized conditions suggested the intermediacy of a highly polar intermediate. Whether this intermediate is a highly polarized complex (charge-transfer complex or exciplex) or an ion pair resulting from electron transfer cannot be established on the basis of the presently available data. In view of the correlation between the log k_q for naphthalene fluorescence quenching by highly strained hydrocarbons and the oxidation half-wave potential for these same hydrocarbons, we will utilize the concept of ion-pair formation for the sake of mechanistic discussions in this communication. Electron transfer from **3** to excited state 1-cyanonaphthalene (1-CN) could produce **12** and 1-CN$^{-}\cdot$. This is reasonable in view of the excited-state reduction potential of 1.83 V for 1-CN. The cation radical, **12**, would be expected to be extremely reactive, but structurally stable.[11] Addition of methanol to **12** would produce a new cation radical which could accept an electron back either from 1-CN$^{-}\cdot$ or from a second molecule of starting material[12] to produce **13** or a related precursor of **11**. Utilization of methanol-*O-d* as solvent resulted in 100% incorporation of one deuterium, which indicated that the source of the hydrogen which was added to **3** was the hydroxyl proton.

The clean photosensitized addition of methanol to **3** prompted us to investigate the use of other nucleophiles. When 10% aqueous tetrahydrofuran containing 0.1% potassium hydroxide was used as solvent, **14** was obtained in 90% (VPC yield vs. an internal standard, isolated yield 50%).[13] When the irradiation was carried out on a 40:1 acetonitrile 2,2,2-trifluoroethanol solution of **3**, 1-CN,[14] potassium cyanide, and 18-crown-6, **15** was obtained in 91% yield, mp 31-32 °C.[6] The structure of **15** was established on the basis of comparison of its ^1H NMR and ^{13}C NMR spectra with those of **11** and **14**.

In summary, we have demonstrated that the quenching of fluorescence by *saturated* hydrocarbons can result in productive and interesting photochemical conversion of these hydrocarbons. To our knowledge, the addition reactions described above represent the first examples of photosensitized additions of nucleophiles to hydrocarbons in the absence of activating aryl substituents or other π systems attached directly to the hydrocarbon skeleton.[15] As part of our studies of the oxidation of strained hydrocarbons,[2] we have measured the oxidative half-wave potentials of approximately 40 compounds which would be predicted to quench fluorescence of various naphthalene and anthracene derivatives. It is anticipated that many of these compounds will undergo interesting and useful photosensitized reactions. We are continuing to explore this area.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231, which supported this investigation.

---

(8) The potassium hydroxide was added to avoid any acid-catalyzed side reaction of **3**, which is extremely acid sensitive. In the absence of base, the photosensitized reaction gave a mixture of **11** and 2-methoxybicyclo[4.1.0]heptane (the normal product of acid-catalyzed addition of methanol to **3**).[9] Control experiments established that the fluorescence of 1-cyanonaphthalene was not quenched under our reaction conditions in the absence of **3**. This ruled out electron transfer from methoxide to the sensitizer, followed by attack of the methoxyl radical on **3**.

(9) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571.

(10) Müller, E. *Tetrahedron Lett.* **1973**, *1201*, 1203. Müller, E. *Chem. Ber.* **1975**, *108*, 1401.

(11) Theoretical calculations indicate that the cation radical generated by removal of an electron from bicyclo[1.1.0]butane should maintain a structure which is very similar to the parent hydrocarbon. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793.

(12) The latter possibility would require the involvement of a photoinduced chain reaction. The observation of a quantum yield of 0.22 for product formation and a quantum yield of 0.89 for fluorescence quenching of $3 \times 10^{-2} - 3 \times 10^{-3}$ M 1-CN in methanol containing 10^{-1} M **3** suggests the absence of a chain reaction but does not rigorously exclude such a possibility. Clearly, only a small portion of the fluorescence quenching leads to the chemical transformation of **3**. A photoinduced chain reaction has been observed in a related system by Mukai and co-workers.[3]

(13) The structure of **14** was established through comparison with an independently synthesized authentic sample.[10] The sample of **14** prepared photochemically had mp 124-126 °C (lit.[10] mp 109-124 °C). The sharp melting point is attributed to the excellent stereochemical purity of the photosensitized addition.

(14) The log k_q for the fluorescence quenching of 1-CN by **3** in acetonitrile was 10.06. Under these conditions the process appeared to be diffusion controlled.

(15) In some respects the additions to saturated C-C bonds described in this communication are reminiscent of the sensitized additions of various nucleophiles to the double bond of 1-phenylalkenes studies by Arnold and co-workers: Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. See also: Arnold, D. R.; Humphreys, R. W. R. *Ibid.* **1979**, *101*, 2743.

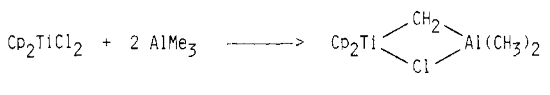
Synthesis and Characterization of "Long-Chain" Alkylidene-Bridged Hetero Bimetallic Complexes

Frederick W. Hartner, Jr., and Jeffrey Schwartz*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received March 16, 1981
Revised Manuscript Received June 16, 1981

Alkylidene-bridged binuclear complexes of transition metals are currently undergoing active study as models for intermediates in the Fischer-Tropsch process[1] or olefin metathesis[2] or as reagents for alkylidene transfer. Early interest in this field derived from observations of reactions between Cp_2TiCl_2 and trimethylaluminum.[3] A major advance in this area occurred when Tebbe and co-workers isolated, identified, and characterized a series of compounds of general structure **1** from this type of reaction (reaction 1).[4] It was noted that such compounds could participate



$$\mathrm{Cp_2TiCl_2} + 2\ \mathrm{AlMe_3} \longrightarrow \mathrm{Cp_2Ti}\begin{smallmatrix}\mathrm{CH_2}\\ \\ \mathrm{Cl}\end{smallmatrix}\mathrm{Al(CH_3)_2}$$

1

---

(1) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *Ibid.* **1979**, *101*, 4128. Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *Ibid.* **1980**, *102*, 1752. Herrman, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *Ibid.* **1980**, *102*, 5906. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(2) Garnier, F.; Krausz, P. *J. Mol. Catal.* **1980**, *8*, 91. Rudler, H. *Ibid.* **1980**, *8*, 53.

(3) Heins, E.; Hinck, H.; Kaminsky, W.; Oppermann, G.; Raulinat, P.; Sinn, H. *Makromol. Chem.* **1970**, *134*, 1.