(KBr) 3350, 2938, 2846, 1740, 1680, 1260, 1045 cm^{-1}. Anal. Calcd for $C_{318}H_{544}O_{88}N_{16}$: C, 63.64; H, 9.14; N, 3.74. Found: C, 63.28; H, 8.96; N, 3.77.

1,3,5,7-Tetrakis{[*N*-[3-[[*N*-[3-carboxy-1,1-bis(2-carboxyethyl)propyl]amino]carbonyl]-1,1-bis[2-[[*N*-[3-carboxy-1,1-bis(2-carboxyethyl)propyl]amino]carbonyl]ethyl]propyl]amino]carbonyl}adamantane (14). A solution of ester **13** (150 mg, 25 μmol) in formic acid (96%, 2 mL) was stirred at 25 °C for 20 h. Workup and purification, similar to that of acid **12**, gave (95%) acid **14**, as a very hygroscopic solid:[31] mp 350–354 °C dec; ^{1}H NMR (D_2O) δ 1.80 (s, CH_2, 12 H), 2.18–2.41 (m, CH_2, 192 H); ^{13}C NMR (D_2O) δ 30.2 (CCH_2CH_2COOH), 30.8, 31.6 (CCH_2CH_2CONH), 39.1 (β-CH_2), 42.8 (α-C), 58.1 (CCH_2CH_2CONH), 58.5 (CCH_2CH_2COOH), 178.0 (COOH), 180.2 (CONH); IR (KBr) 3360, 3340–2600, 2920, 1745, 1685, 1240, 1060 cm^{-1}.

Acknowledgment. We thank the National Science Foundation (DMR 86-00929; 89-06792) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for Partial support of this research.

Registry No. 1, 137494-80-5; 2, 53120-57-3; 3, 100884-80-8; 4, 101892-34-6; 5, 137494-81-6; 6, 137494-82-7; 7, 136586-93-1; 8, 137515-52-7; 9, 137494-83-8; 10, 136586-99-7; 10 (homopolymer), 137467-21-1; 11, 137494-84-9; 12, 137494-85-0; dimethyl malonate, 108-59-8; formaldehyde, 50-00-0; dibromomethyl, 74-95-3; diethyl malonate, 105-53-3; tris, 77-86-1; hexaethyl 1,1,3,3,5,5-pentanehexacarboxylate, 80311-87-1.

---

[31] Purity was judged to be >95% based on ^{13}C NMR spectral data.

Relatively Stable *N*-Benzhydryl- and *N*-Benzyldiarylketene Imines and Their Conversion to Cyanodiarylmethanes via an Isolable Radical

Leo F. Clarke, Anthony F. Hegarty,* and Pat O'Neill

Chemistry Department, University College Dublin, Dublin 4, Ireland

Received June 12, 1991

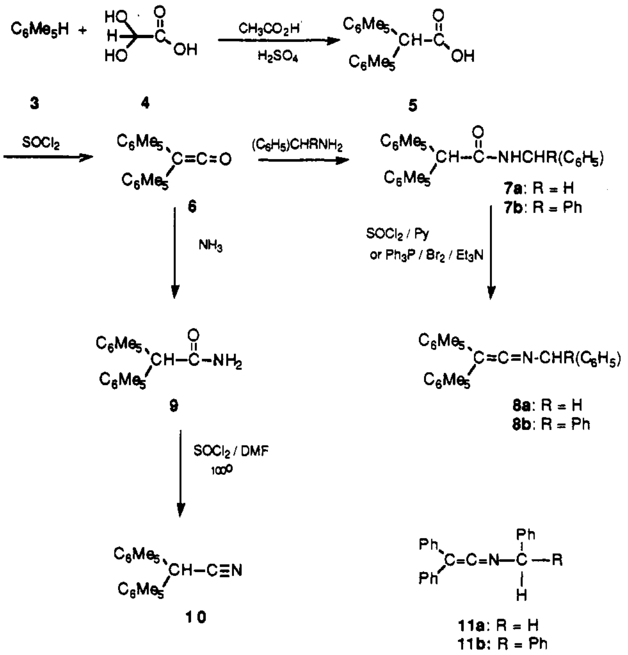
An efficient synthetic route to the sterically hindered ketene imines *N*-benzyl- and *N*-benzylhydrylbis(pentamethylphenyl)ketene imines **8** from dipentamethylphenyl ketene **6** is described. The thermal stability of these ketene imines is in marked contrast to the diphenylketene imine analogues which rearrange rapidly to C-trisubstituted nitriles. On heating **8b** is converted to the relatively stable free radical **13** which can be reduced to the nitrile **10** in a variety of solvents. These radicals are proposed intermediates in the ketene imine–nitrile rearrangement, and the mechanism of this reaction is considered in terms of these results.

The conversion of ketene imines **1** to nitriles **2** is known to occur with varying degrees of ease and through competing reaction pathways depending on the nature of substituents R^1, R^2, and R^3.

N-Stannylketene imines, for example, are known to react with a variety of reagents which cleave the nitrogen–tin bond to generate nitriles in high yield.[1] The photochemical conversion of *N*-methylarylketene imine to a trisubstituted acetonitrile has also been reported.[2,3] *N*-*tert*-Butyldiphenylketene imine, on the other hand, undergoes a disproportionation reaction at 125 °C to yield diphenylacetonitrile, *tert*-butyl chloride, and isobutylene.[4] The *N*-(arylmethyl)diphenylketene imine system has also been noted for its ease of ketene imine to nitrile conversion. The modest temperatures (25–65 °C) required to induce thermal rearrangement and the good yield of nitrile has made this system a prime candidate for mechanistic investigations.[5]

Singer et al. have shown[5,6] through kinetic, stereochemical, and trapping experiments involving *N*-benzyl- and other *N*-(arylmethyl)diphenylketene imines that this thermal [1,3] nitrogen to carbon rearrangement proceeds via a free-radical mechanism. On the basis of their accumulated results they concluded that the rate-determining step was the homolytic cleavage of the ketenimine's N–R$_3$ bond to form a cage radical pair which subsequently recombines to nitriles.

Scheme I



Because of our continued interest in understanding the effects of bulky aromatic groups on unstable reaction intermediates[7,8] we have now investigated the influence of

---

[1] Miller, E.; Sommer, R.; Neumann, W. P. *Liebigs Ann. Chem.* **1968**, *718*, 11.

[2] Kagen, H.; Lillien, I., *J. Org. Chem.* **1966**, *31*, 3728.

[3] Selvarajan, R.; Boyer, J. H. *J. Chem. Soc., Chem. Commun.* **1970**, 889.

[4] Ciganek, E. *Tetrahedron Lett.* **1969**, 5179.

[5] Singer, L. A.; Lee, K. W. *J. Chem. Soc., Chem. Commun.* **1974**, 962.

[6] Lee, K. W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

0022-3263/92/1957-0362$03.00/0

geminal pentamethylphenyl groups, C_6Me_5, on the reactivities on *N*-benzyl- and *N*-benzhydryldiphenylketene imines. Such a modification to the structure of these thermally labile ketene imines was envisaged to hinder [1,3] nitrogen to carbon rearrangement to nitriles due to the steric hindrance imposed by the pentasubstituted aryl groups.[8,9]

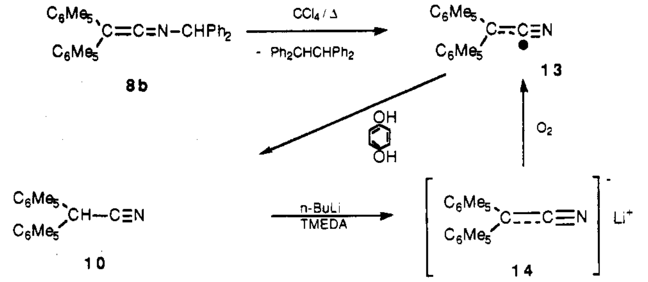
N-(Arylmethyl)bis(pentamethylphenyl)ketene imines **8** were synthesized as shown in Scheme I. The key intermediate is bis(pentamethylphenyl)acetic acid (**5**), which is one of the most hindered carboxylic acids known.[10] Its optimum preparative conditions involves the acid-catalyzed Friedel–Crafts reaction of pentamethylbenzene (**3**) with glyoxylic acid hydrate (**4**) in a sulfuric acid/acetic acid mixture (2:3); this gives **5** in 71% yield. This reaction requires careful control of temperature and acidity due to the facile reduction of pentamethylmandelic acid, an intermediate in the reaction.[11] Small quantities of monoarylacetic acid can be removed from **5** by recrystallization from 1-propanol in which it has a preferential solubility. The conversion of **5** to the bis(pentamethylphenyl)ketenes **6** was accomplished in one pot (78%). The steric hindrance created by the C_6Me_5 groups is reflected not only in the remarkable stability of **6** (which can be stored at ambient temperature indefinitely without decomposition[12]) but also by the instability of the acid chloride of **5** which spontaneously undergoes dehydrochlorination to **6** due to the relief of significant *B*-strain.[13]

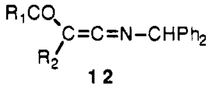
By treating the diarylketene **6** with 3 mol equiv of the appropriate amine in refluxing toluene it was possible to synthesize *N*-(arylmethyl)bis(pentamethylphenyl)acetamides **7**. The conversion of the *N*-benzylamide **7a** to its corresponding ketene imine was accomplished in 62% yield by its in situ bromination/dehydrobromination with $Ph_3P/Br_2/Et_3N$ in refluxing dichloromethane. This method, however, was not generally applicable in that for the *N*-benzhydryl amide **7b** the ketene imine was not obtained but rather the bis(pentamethylphenyl)acetonitrile (**10**). This unexpected product was isolated in modest yield from the red/purple solution (the color faded within 2–3 h). There was no evidence (IR) for the ketene imine **8** in the crude product.

However, by applying much milder reaction conditions we have also synthesized the *N*-benzhydrylketene imine (**8b**). Chlorination/dehydrochlorination of *N*-(diphenylmethyl)bis(pentamethylphenyl)acetamide (**7b**) in $SOCl_2$/Py at ambient temperature and chromatographic purification followed by recrystallization from ether/methanol without the application of heat gave *N*-(diphenylmethyl)bis(pentamethylphenyl)ketene imine (**8b**) as a white crystalline product in 30% yield.

To the best of our knowledge, **8b**, which shows the characteristic ketene imine absorption, $\nu(C{=}C{=}N) = 2010$ cm^{-1}, is the first isolable *N*-benzhydryl ketene imine. The corresponding *N*-(diphenylmethyl)diphenylketene imine (**11b**) is very labile. Although spectral evidence for this ketene imine was obtained on analyzing the crude reaction mixture the only product isolated after chromatography was the rearranged nitrile, 2,2,3,3-tetraphenylpropionitrile.[6,14] *N*-(Diphenylmethyl)acylketene imines **12** (R^1 = H, Ph; R^2 = Me, Ph) also decompose on attempted isolation. Again, IR data for its presence is obtained when the reaction mixture is quickly analyzed.[15]

Scheme II





$R_1CO(R_2)C{=}C{=}N{-}CHPh_2$

12

The thermal stability of *N*-(phenylmethyl)bis(pentamethylphenyl)ketene imine (**8a**) is in marked contrast to that for the corresponding *N*-(phenylmethyl)diphenylketene imine (**11a**). The latter compound afforded 1,1,2-triphenylpropionitrile in ca. 90% yield when heated to 60 °C in CCl_4.[5] Its bis(pentamethylphenyl) equivalent **8a**, however, was recovered in quantitative yield after it had been refluxed for 1 h in toluene. There was no color change in the solution. Neither was there any detectable change in color when the neat ketene imine was heated in excess of 200 °C (mp 92–94 °C) on a hot-stage melting point apparatus while viewed under a microscope. Clearly, the presence of pentamethylphenyl groups increase the thermodynamic stability of *N*-benzyl- and *N*-benzhydrylketene imines. A stronger C–N bond is less likely to undergo homolytic cleavage. This would be a direct result of the steric effects of the C_6Me_5 groups which would prevent extended resonance delocalization and the electronic effects of the C_6Me_5 group whose electron-donating contribution to the heterocumulene system would also be felt by the C–N bond.

N-(Diphenylmethyl)bis(pentamethylphenyl)ketene imine (**8b**) does not have a sharp melting point (111–118 °C), and melting is accompanied by the appearance of a dark red coloration. Furthermore, when this ketene imine was heated to 40–50 °C in a range of solvents, a dark red/purple color developed. The intensity of this color is related to temperature, and the half-life for formation is dependent on the nature of the solvent. Regenerating this purple coloration after its fading could be repeated until the ketene imine present was depleted. Analysis of the solution at this stage revealed bis(pentamethylphenyl)acetonitrile (**10**). The addition of quinol catalyzed the apperance of the acetonitrile **10** as the purple color was replaced by the yellow color of quinone.

An ESR spectrum of a solution prepared in the above manner confirmed that the purple color was that of the free radical, cyanobis(pentamethylphenyl)methyl (**13**, Scheme II). This spectrum ($g = 2.0037$; CCl_4) consisted of a single broad line which revealed complex hyperfine interactions with a basic three line pattern as expected for

---

[7] O'Neill, P.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1987**, 744.

[8] O'Neill, P.; Hegarty, A. F. *J. Org. Chem.* **1987**, *52*, 2113.

[9] Hegarty, A. F.; O'Neill, P. *Tetrahedron Lett.* **1987**, *28*, 901.

[10] O'Neill, P. Ph.D. Thesis, NUI, 1988.

[11] We have successfully synthesized **5** in high yield from pentamethylmandelic acid and pentamethylbenzene under the same reaction conditions.

[12] Diphenylketene, in comparison, needs to be stored in tightly stoppered bottles at <0 °C in order to prevent decomposition (*Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 356).

[13] Tidwell, T. T. *Tetrahedron* **1987**, *34*, 1855.

[14] Lee, K. W.; Singer, L. A. *J. Org. Chem.* **1974**, *39*(25), 3780.

[15] An IR spectrum of the THF solution taken in the absence of oxygen showed two absorptions, 2044 and 2080 cm^{-1} (shoulder peak). These values coincide with ν_{as} (C—C≡N) = 2065 cm^{-1} reported for α-cyanobenzyllithium: Boche, G.; Marsch, M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 373.

a radical whose unpaired electron is delocalized onto the cyano nitrogen atom; its IR spectrum (CCl_4) showed ν-($C{\equiv}N$) = 2120 cm^{-1} (compared with that of the nitrile **10**; ν($C{\equiv}N$) = 2230 cm^{-1}). We therefore conclude that *N*-(diphenylmethyl)bis(pentamethylphenyl)ketene imine (**8b**) thermally decomposes to a stable free radical, cyanobis-(pentamethylphenyl)methyl (**13**, and presumably 1,1,2,2-tetraphenylethane and/or diphenylmethane). A rearrangement for **8** analogous to **1** → **2** is prohibited on steric grounds by the C_6Me_5 groups, which in turn provides the necessary kinetic stability for its corresponding radical **13**.

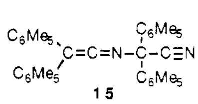
To verify that cyanobis(pentamethylphenyl)methyl radical **13** was the initial product of the thermal decomposition of **8b** an unambiguous synthetic route to the radical was considered (Scheme II). The C–H precursor to the radical, bis(pentamethylphenyl)acetonitrile (**10**), was synthesized from bis(pentamethylphenyl)ketene in 42% yield (Scheme I). This nitrile was found to undergo slow proton transfer and only under the strongly basic conditions of 3 mol equiv of *n*-BuLi TMEDA was it quantitatively deprotonated. Under an inert atmosphere it was possible to observe the orange solution of lithium diarylacetonitrile **14**.[16] Oxidation of the α-cyano "carbanion" **14** to the radical **13** was accomplished by permitting atmospheric oxygen to enter the reaction vessel. After an induction period of 5–10 min, during which time residual *n*-BuLi reduced the radical back to **14**, the reaction mixture went dark purple in color. Pouring the contents of the flask into water brought about the precipitation of cyanobis(pentamethylphenyl)methyl radical **13** as a dark crimson powder as the major product.

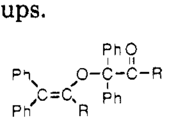
This radical showed unusual stability. While it was not indefinitely stable in the solid state (its C–H precursor was regenerated within 1–2 months), its stability in solution depended on the H-donating power of the solvent. In THF, for example, its half-life was several minutes while in CCl_4 solution it was several hours at 25 °C. In the presence of quinol it was rapidly reduced to **10** with complete discharge of its color.

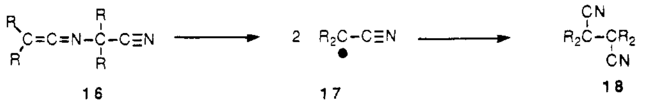
Agreement in the spectroscopic and analytical results for the isolated radical and the product formed from the thermal decomposition of **8b** confirmed their identity.

The IR spectrum of the precipitated radical generated from the oxidation of the lithio compound **14** substantiated the TLC result that the product was not pure. The ν-($C{\equiv}N$) = 2229 cm^{-1} absorption is consistent with the presence of bis(pentamethylphenyl)acetonitrile, while we assign the absorption peaks at 2189 and 2008 cm^{-1} as those of the cyano and heterocumulene moieties of the radical dimer **15** (although this product was not actually isolated). Analogous radical dimers have been reported, e.g., *N*-(α-cyanoalkyl)dialkylketene imine **16** (R = CH_3, $-(CH_2)_4-$). This heterocumulene yields the succinonitrile derivative **18** in high yield at 80–100 °C via the α-cyanomethyl radical **17**.[16,17]

Tetraphenylsuccinonitrile (**18**, R = Ph) dissociates readily on heating (ca. 50 °C) in an inert solvent to form cyanodiphenylmethyl (**17**, R = Ph).[18] The ESR spectrum for **17** (R = Ph), $g = 2.0028$, $a_N = 2.0$ G, suggests less interaction between the unpaired electron and its cyano nitrogen atom than that reported for **13**. This is probably a result of greater resonance delocalization of the radical character with the phenyl groups.


15


19


16 **17** **18**

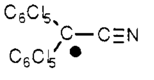
The C–N mode of dimerisation for **13** could be attributed to both steric factors and substantial radical ketene iminyl character. This applies in the case of α-benzoyl-, α-acetyl-, and α-formyldiphenylmethyl radicals which show unusual C–O coupling to give enol ether **19**. The different dimer structure to **16** or **18** (R = Ph) is due to their high enoxyl character. This is reflected in their *g* values of 2.0033, 2.0037, and 2.0040, respectively.[19] These values compare well with the *g* value of 2.0036 for **13**.

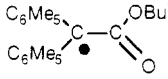
There is a considerable reduction in the dipentamethylphenyl radical's **13** cyano absorption, ν($C{-}C{=}N$) = 2116 cm^{-1} relative to that in bis(pentamethylphenyl)-acetonitrile. In fact, this difference of more than 100 cm^{-1} is equivalent to the difference between the radical **13** and a ketene imine such as *N*-methylbis(pentamethylphenyl)ketene imine, ν($C{=}C{=}N$) = 2016 cm^{-1}.[20]

This is indicative of a considerable degree of resonance delocalization of the radical onto nitrogen giving it some ketene iminyl character. The ESR spectrum of the isolated radical **13** ($g = 2.0036$; CCl_4) is also consistent with a considerable degree of interaction between the unpaired electron and the cyano group.

It is widely agreed that steric factors are more important in the stabilization of a radical than are electronic effects.[21] The triphenylmethyl radical, for example, is stable only in dilute solution and is susceptible to both oxidation and dimerization. The perchlorinated triarylmethyl analogue however, has been termed an "inert free radical" due to its exceptional stability. This has been attributed to purely steric factors as the corresponding carbocation and carbanion have comparable stabilities.[22]

Cyanobis(pentachlorophenyl)methyl (**19**), prepared by oxidation of its corresponding anion with iodine, is a purple air-stable solid. The half-life of this radical in a H-donating solvent such as THF is measured in terms of days. It is reduced to its corresponding diarylacetonitrile.[9]


19


20

The ESR spectrum of **19** ($CHCl_3$) consists of three lines with $g = 2.0047$ and $a_N = 5.99$ G. These values are typical of radicals with considerable delocalization onto a nitrogen atom. This cyano radical did not show a ν($C{\equiv}N$) absorption in its IR spectrum probably due to the strong electron withdrawing effect of the Cl_5C_6 groups. Its C–H precursor had only a very weak ν($C{\equiv}N$) at 2253 cm^{-1}.[9]

The radical **20**, synthesized by the treatment of its corresponding ester with *n*-butyllithium in the presence

---

[16] (a) Wu, C. S.; Hammond, G. S.; Wright, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 5386. (b) Hammond, G. S.; Wu, C. S.; Trapp, O. D. Warkentin, J.; Keys, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 5394. (c) Waits, H. D.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 1911.

[17] de Vries, L. *J. Org. Chem.* **1973**, *38*, 4357.

[18] (a) Wittig, G.; Pockels, U. *Ber.* **1936**, *69*, 790. (b) Wittig, G.; Petri, H. *Liebigs Ann. Chem.* **1934**, *513*, 26. (c) Wittig, G.; Hopf, H. *Ber.* **1932**, *65*, 760.

[19] Neumann, W. P.; Stapel, R. *Chem. Ber.* **1986**, *119*, 3422.

[20] Clarke, L. F.; Hegarty, A. F. Unpublished results.

[21] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; p 162ff.

[22] (a) Ballester, M.; Riera-Figueras, J.; Rodriguez-Sivrana, J. *Tetrahedron Lett.* **1970**, 3615. (b) Ballester, M.; de la Fuente, G. *Ibid.* **1970**, 4509. (c) Ballester, M.; Veciana, J.; Riera, J.; Gastaner, J.; Rovira, C.; Armet, O. *J. Org. Chem.* **1986**, *51*, 2472.

of oxygen, is an indefinitely stable purple solid which does not react with oxygen or dimerize. Like cyanobis(pentamethylphenyl)methyl radical (**13**) the stability of this radical is ascribed mainly to steric factors but its IR and ESR (g = 2.0041; CCl_4) data also indicate considerable stabilization by its α-functional group.[7]

Conclusion

On the basis of stereochemical data, the observation of a CIDNP, and solvent effects, Singer and co-workers[5,6,14] concluded that the rearrangement of *N*-arylalkylketene imines to nitriles occurs via a proximate radical pair (rather than via an ion pair or a concerted mechanism). This was also consistent with the partial retention of structure of the migrating group and the observation of some dimerization products. We have shown that when the C-aryl terminus of the ketene imine is replaced by the very bulky dipentamethylphenyl group, although the formation of kinetically stable similar radicals following C–N bond homolysis is possible, the rates of formation of these radicals are very much reduced relative to the rate of rearrangement.

Experimental Section

Melting point values were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 FT spectrometer while ^1H NMR were obtained on a Jeol JNM-GX 270 spectrometer operated at 270 MHz. Commercial reagents were used without further purification unless otherwise stated.

Bis(pentamethylphenyl)acetic Acid. Pentamethylbenzene (101.65 g, 0.68 mol) and glyoxylic acid hydrate (22.38 g, 0.25 mol) were dissolved in 323 mL of warm acetic acid. This mixture was cooled in an ice bath, and concentrated sulfuric acid (198 mL) was added over 0.75 h. The resulting thick red suspension was stirred at ambient temperature for 2 days. This was then poured into 1 L of water, and the product was extracted with 1 L of ether. After being washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$, the organic solution was evaporated to dryness. The crude product was recrystallized from 1-propanol to afford 61.2 g (71%) of bis(pentamethylphenyl)acetic acid: mp 254–256 °C; δ ($CDCl_3$) 2.07 (s, 12 H), 2.18 (s, 12 H), 2.23 (s, 6 H), 5.60 (s, 1 H), 10.95 (s, 1 H, exchangeable); ν_{max} (KBr) 3325 (OH), 2926 (CH), 1704 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 82.30; H, 9.42.

Bis(pentamethylphenyl)ketene. Thionyl chloride (2 mL, 27.2 mmol) was added to a cold suspension of bis(pentamethylphenyl)acetic acid (8 g, 22.7 mmol) in 80 mL of dry toluene. Two drops of pyridine were added, and the mixture was refluxed for 1.5 h. The hot solution was then treated twice with charcoal and filtered. After rotary evaporation of the solvent the crude product was recrystallized from acetonitrile to yield bis(pentamethylphenyl)ketene (5.92 g, 78%) as bright yellow crystals: mp 153–156 °C; δ ($CDCl_3$) 2.15 (s, 12 H), 2.21 (s, 12 H), 2.25 (s, 6 H); ν_{max} (KBr) 2917 (CH), 2093 (C=C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 80.28; H, 9.06.

***N*-(Diphenylmethyl)bis(pentamethylphenyl)acetamide.** Diphenylmethylamine (15.6 g, 85.1 mmol) and crude bis(pentamethylphenyl)ketene, prepared from bis(pentamethylphenyl)acetic acid (10 g, 28.4 mmol), were dissolved in 250 mL of dry toluene and the resulting dark red solution was refluxed for 1 h. This was then poured into a 1:1 mixture of toluene/water (250 mL), and the organic phase was washed with 5% H_2SO_4 (4 × 250 mL), 5% $NaHCO_3$ (2 × 250 mL), and saturated aqueous NaCl and finally dried with anhydrous $MgSO_4$. Evaporation of the solvent gave a pale yellow solid which was purified by flash chromatography (1:5 ether/petroleum ether (60–80 °C) eventually increasing the strength of the eluent to pure ether in order to remove the desired product) followed by recrystallization from propanol/water. This gave *N*-(diphenylmethyl)bis(pentamethylphenyl)acetamide (6.79 g, 46% based on the corresponding carboxylic acid) as white needle-like crystals: mp 196–197 °C; δ ($CDCl_3$) 1.96 (s, 12 H), 2.15 (s, 12 H), 2.23 (s, 6 H), 5.47 (s, 1 H), 6.39 (s, 1 H), 7.0–7.3 (m, 10 H); ν_{max} (KBr) 3420 (NH), 1667 (C=O) cm^{-1}. Anal. Calcd for $C_{37}H_{43}NO$: C, 85.83; H, 8.37; N, 2.71. Found: C, 85.54; H, 8.50; N, 2.53.

Similarly prepared was the following.

***N*-(Phenylmethyl)bis(pentamethylphenyl)acetamide:** white microcrystals (ex ethylacetate/petrol (60–80 °C)); yield 30%; mp 216–218 °C; δ ($CDCl_3$) 1.98 (s, 12 H), 2.18 (s, 12 H), 2.22 (s, 6 H), 4.49 (d, 2 H, J = 5.68 Hz), 4.97 (s, 1 H), 5.90 (1 H, br), 7.20–7.36 (m, 5 H); ν_{max} (KBr) 3415, 3278 (NH), 1645 (C=O) cm^{-1}. Anal. Calcd for $C_{31}H_{39}NO$: C, 84.30; H, 8.90; N, 3.17. Found: C, 84.22; H, 9.08; N, 2.94.

***N*-(Diphenylmethyl)bis(pentamethylphenyl)ketene Imine.** Thionyl chloride (0.23 g, 1.97 mmol) was added to a solution of *N*-(diphenylmethyl)bis(pentamethylphenyl)acetamide (1.02 g, 1.97 mmol) in 10 mL of dry pyridine. The initially colorless solution became yellow and then orange with the precipitation of pyridine hydrochloride while the reaction mixture was stirred at ambient temperature for 30 min. The contents of the flask were then poured into a mixture of 1:1 petroleum ether (60–80 °C)/water (50 mL), and the organic phase was washed well with water (unreacted amide remains at the interface) and saturated NaCl and finally dried with anhydrous $MgSO_4$. To isolate the desired product by flash chromatography ca. 5 g of silica gel was added to the petrol solution of the crude product before the solvent was removed under reduced pressure. The resulting powder was then added to a conditioned chromatographic column and eluted with 1:19 ether/petroleum ether (40–60 °C). The progress of the elution was facilitated by the dark red band of the radical bis(pentamethylphenyl)cyano methyl which immediately followed the desired product. A pale pink crystalline solid was isolated from the fraction preceeding this dark red band. Its recrystallization from ether/methanol (without the application of heat) afforded *N*-(diphenylmethyl)bis(pentamethylphenyl)ketene imine (0.28 g, 30%) as colorless crystals: mp 111–118 °C dec; δ ($CDCl_3$) 2.05 (s, 12 H), 2.15 (s, 12 H), 2.22 (s, 6 H), 5.95 (s, 1 H), 7.2–7.3 (m, 10 H); ν_{max} (KBr) 2010 (C=C=N) cm^{-1}. Anal. Calcd for $C_{37}H_{41}N$: C, 88.93; H, 8.27; N, 2.80. Found: C, 88.81; H, 8.31; N, 2.59.

***N*-(Phenylmethyl)bis(pentamethylphenyl)ketene Imine.** Bromine (0.2 mL, 3.9 mmol), dry triethylamine (2.7 mL, 19.7 mmol), and then *N*-(phenylmethyl)bis(pentamethylphenyl)acetamide (1.74 g, 3.9 mmol) were added to an ice-cold solution of triphenylphosphine (1.03 g, 3.9 mmol) in 50 mL of dry dichloromethane. When the yellow solution had reached ambient temperature it was refluxed for a further 2 h. Sufficient silica gel was then added for the reaction mixture to cake. Removal of the dichloromethane under reduced pressure left a powder which was flash-chromatographed with 1:9 ether/petroleum (40–60 °C) as eluent. Identifying the product fraction was made easy by its yellow color. From this fraction *N*-(phenylmethyl)bis(pentamethylphenyl)ketene imine (1.04 g, 62%) was isolated as a yellow solid. Its recrystallization from ether/methanol afforded 0.54 g (32%) of white needle-like crystals: mp 92–94 °C; δ ($CDCl_3$) 2.15 (s, 12 H), 2.19 (s, 12 H), 2.25 (s, 6 H), 4.76 (s, 2 H), 7.26 (s, 5 H); ν_{max} (KBr) 2012 (C=C=N) cm^{-1}. Anal. Calcd for $C_{31}H_{37}N$: C, 87.89; H, 8.80; N, 3.31. Found: C, 88.06; H, 9.10; N, 3.19.

Bis(pentamethylphenyl)acetamide. Bis(pentamethylphenyl)ketene (10 g, 30.0 mmol) was dissolved in benzene (250 mL), and anhydrous ammonia was bubbled through the solution for 1 h. The initial yellow solution went red and then orange as a solid precipitated. After residual ammonia was removed with nitrogen the pink solid precipitate was filtered and washed with benzene and finally petroleum (40–60 °C). Recrystallization from absolute alcohol gave bis(pentamethylphenyl)acetamide (6 g, 57%): mp 264–266 °C; δ ($CDCl_3$) 2.10 (s, 12 H), 2.19 (s, 12 H), 2.24 (s, 6 H), 5.43 (s, 1 H), 5.52 (1 H, br), 5.70 (1 H, br); ν_{max} (KBr) 3429, 3304 (NH), 1684, 1655 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{33}NO$: C, 82.00; H, 9.46; N, 3.98. Found: C, 81.84; H, 9.79; N, 4.32.

Bis(pentamethylphenyl)acetonitrile. Bis(pentamethylphenyl)acetamide (5.5 g, 16 mmol) and thionyl chloride (7.45 g, 63 mmol) were heated to 100 °C in dimethylformamide (55 mL) for 0.5 h. As the amide dissolved the reaction mixture became red and copious HCl was liberated. While still warm, the contents of the flask was poured into a mixture (1:1.7) of water/ether (400 mL). The ether phase was cautiously washed with water, 10%

aqueous Na_2CO_3, and saturated NaCl and finally dried with $MgSO_4$. The crude product was recrystallized from 1-propanol after treatment with charcoal to yield bis(pentamethylphenyl)acetonitrile (3.84 g, 74%) as large needle-like crystals: mp 185–188 °C; δ ($CDCl_3$) 2.13 (s, 24 H), 2.18 (s, 6 H), 5.71 (s, 1 H); ν_{max} (KBr) 2922 (CH), 2223 (C≡N) cm^{-1}. Anal. Calcd for $C_{24}H_{31}N$: C, 86.43; H, 9.37; N, 4.20. Found: C, 86.24; H, 9.50; N, 4.36.

Bis(pentamethylphenyl)cyanomethyl. Method 1. *N*-(Diphenylmethyl)bis(pentamethylphenyl)ketene imine (0.2 g, 0.4 mmol) was dissolved in 5 mL of carbon tetrachloride. This colorless solution was then heated to 50 °C for 30 min, and the resulting dark purple solution was analyzed: TLC (1:9 ether/petroleum (40–60 °C)) R_f 0.38 (purple spot fading within 30 min), none of the starting material was present; ν_{max} (CCl_4) 2120 cm^{-1}; $g(CCl_4) = 2.0037$. Quinol (0.22 g, 2 mmol) was added to the reaction vessel with the immediate change in the solution to the yellow color of quinone. Analysis of this quenched solution confirmed that no starting *N*-benzhydrylketene imine remained. Bis(pentamethylphenyl)acetonitrile, however, was present: TLC (1:9 ether/petroleum (40–60 °C)) R_f 0.36 which is the same as the R_f value for an authentic sample of bis(pentamethylphenyl)acetonitrile; ν_{max} (CCl_4) 2230 cm^{-1}; δ (CCl_4) 2.16 (s, 24 H), 2.18 (s, 6 H), 5.74 (s, 1 H). Therefore, the thermal decomposition of *N*-(diphenylmethyl)bis(pentamethylphenyl)ketene imine yielded α-cyanobis(pentamethylphenyl)methyl and presumably diphenylmethane and/or 1,1,2,2-tetraphenylethane (which were not isolated).

Method 2. Bis(pentamethylphenyl)acetonitrile (0.24 g, 0.72 mmol) in 3 mL of dry THF was sealed by a rubber septum in a round-bottom flask and flushed with anhydrous oxygen-free nitrogen. This was followed by the addition of tetramethylene diamine (0.32 mL, 2.16 mmol) and *n*-butyllithium (1.38 mL, 2.16 mmol) at ambient temperature. The resulting solution went from yellow to orange as it was left stirring for 1 h. A further 5 mL of THF was added to the vessel, and its contents were then exposed to the atmosphere. For the first 5–10 min there was no color change, and then a permanent purple color quickly developed throughout the mixture. After being stirred for a further 10–15 min the solution was poured into 24 mL of water and vigorously stirred until a solid precipitated. This dark crimson powder was collected by filtration, washed with water followed by a little methanol, and dried at 50 °C overnight: TLC (1:9 ether/petroleum (40–60 °C)); R_f 0.34 (purple), 0.45 and a baseline spot; ν_{max} (KBr) 2229, 2189 (C≡N), 2116 (C—C=N), 2008 (C=C=N) cm^{-1}; $g(CCl_4)$ 2.0036. The identified constituents of the crude product were therefore bis(pentamethylphenyl)acetonitrile and α-cyanobis(pentamethylphenyl)methyl, and the third product had a spectrum consistent with that of the dimer *N*-(bis(pentamethylphenyl)cyanomethyl)bis(pentamethylphenyl)ketene imine.

Reductions of α-Cyanobis(pentamethylphenyl)methyl by Quinol and by *n*-Butyllithium. A solution of α-cyanobis(pentamethylphenyl)methyl radical (0.6 g, ~2 mmol) in THF (5 mL) was stirred at ambient temperature. To this red/purple solution was slowly added quinol (1.1 g, 10 mmol). The dark color of the solution was quickly replaced by the yellow color of quinone: TLC (1:9 ether/petroleum (40–60 °C)) $R_f = 0.32$, identified as the corresponding diarylacetonitrile (together with other spots none of which were purple in color (indicating residual radical)).

α-Cyanobis(pentamethylphenyl)methyl (0.6 g, ~2 mmol) was dissolved in 5 mL of dry THF. This solution was deoxygenated and cooled to −16 °C. *n*-Butyllithium (1.6 mL, 2.5 mmol) in hexane was slowly added by syringe. The red-purple color of the radical solution was replaced by the orange color of α-cyanobis(pentamethylphenyl)methyllithium as the solution was allowed to reach ambient temperature. After 15 min, acetic acid (0.16 g, 2.6 mmol) in dry THF (1 mL) was added and the reaction mixture was analyzed: TLC (1:9 ether/petroleum (40–60 °C)) R_f 0.28; this spot which appeared to be the main component of the reaction mixture was identified as bis(pentamethylphenyl)acetonitrile by comparison with an authentic sample.

Registry No. **3**, 700-12-9; **4**, 563-96-2; **5**, 107846-81-1; **6**, 112752-37-1; **7a**, 137122-88-4; **7b**, 137122-89-5; **8a**, 137122-90-8; **8b**, 137122-91-9; **9**, 137122-92-0; **10**, 137122-93-1; **13**, 137122-94-2; benzenemethaneamine, 100-46-9; α-phenylbenzenemethaneamine, 91-00-9.

Nuclear Spin–Spin Coupling via Nonbonded Interactions. 7. Effects of Molecular Structure on N–F Coupling[1]

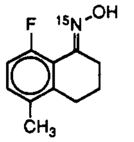
Frank B. Mallory,*,[2a] Eddie D. Luzik, Jr.,[2a] Clelia W. Mallory,[2b] and Patrick J. Carroll[2b]

Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, and Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

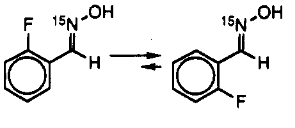
Received January 2, 1991

To test whether the recently discovered phenomenon of through-space nuclear spin–spin coupling between intramolecularly crowded ^{15}N and ^{19}F nuclei shows the same sort of striking dependence on molecular structure as the long-known phenomenon of through-space nuclear spin–spin coupling between pairs of intramolecularly crowded ^{19}F nuclei, several ^{15}N-enriched oximes and some simple derivatives thereof were synthesized and their J_{NF} values were determined by ^{19}F NMR spectroscopy. The experimental J_{NF} values ranged from 8.6 to 43.5 Hz. The molecular structures of these compounds were determined by single-crystal X-ray diffraction. The observed dependence of the ^{15}N–^{19}F coupling constants on molecular structure was qualitatively consistent with the predictions of the lone-pair orbital overlap theory that was developed earlier to account for through-space coupling involving fluorine nuclei.

In part 5 of this series,[3] we reported the first example of "through-space" spin–spin coupling between ^{15}N and ^{19}F nuclei. In that earlier work, we found that oxime **1** has the exceptionally large J_{NF} value of 22.4 Hz, whereas oxime **2**, which possesses the same bond connectivity as **1** but lacks the close spatial proximity between the nitrogen and fluorine atoms that is enforced in **1** by tethering, has a J_{NF} value of only 3.2 Hz.



1: $J_{NF} = 22.4$ Hz



2: $J_{NF} = 3.2$ Hz

---

[1] (a) For part 6, see: Mallory, F. B.; Mallory, C. W.; Baker, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 2577. (b) Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 31, 1987, ORGN-121 and the 23rd Middle Atlantic Regional Meeting of the American Chemical Society, Cherry Hill, NJ, May 25, 1989. (c) Taken from the Ph.D. dissertation of Eddie D. Luzik, Jr., Bryn Mawr College, 1991.

[2] (a) Bryn Mawr College. (b) University of Pennsylvania.

[3] Mallory, F. B.; Mallory, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 4816.

0022-3263/92/1957-0366$03.00/0