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Nitro Olefins and Organoaluminum Compounds: A Powerful Synthetic Tool in Organic Chemistry

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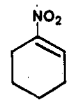
$[R_3AlR']M$ species react with α-nitro olefins showing an unusual aptitude for a preferential transfer of saturated alkyl groups; $[R_2AlR'_2]M$ (R′ = phenyl, benzyl, allyl) species, on the other hand, are able to transfer unsaturated groups with high chemoselectivity. In particular, dialkyldiallylalanates react with α-nitro olefins to give either δ-nitro olefins or the corresponding γ,δ-unsaturated ketones in very good yields. This reaction, synthetically equivalent to the regioselective allylation of carbonyl compounds, was used for the synthesis of allylrethrone, a component of insecticidal synthetic pyrethroid. Only the ether-free diethylalkynylalanes are able to transfer alkynyl groups with ≥85% chemoselectivity.

In recent publications we have described a simple procedure for the selective conjugate alkyl and alkenyl group transfer to α-nitro olefins (1) using either trialkyl- or diisobutylalkenylalanes, respectively (Scheme I).[1,2] The effectiveness and the high regio- and chemoselectivity showed by the reactions of these organometallic reagents with 1 are not found in reactions of triorganoalanes with other α,β-unsaturated systems.[3]

Nitro compounds, such as 2 and 3, are useful intermediates in organic synthesis;[4] therefore, the reactivity of compounds 4–8 toward other organoalane derivatives has been tested in order to better settle the synthetic application of the reported process. In this context mixed tetraorganoalanate reagents, $[R_3AlR']M$, showed some promising features: they are even more selective than triorganoalanes toward a wide number of electrophiles and they can be easily obtained in situ either from Grignard or alkyllithium reagents.[3] Moreover the use of $[R_3AlR']M$ species could obviate the problem of the unreactivity in ethereal solvents of AlR_3 toward nitro olefins.[5]



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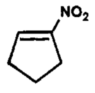

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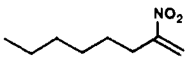

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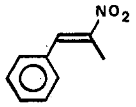

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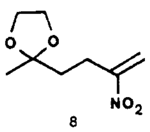

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Results and Discussion

The reactions of 1-nitrocyclohexene with either triisobutylphenyl- or triisobutylallylalanate (**9a,b**), which had been prepared from triisobutylaluminum and phenylmagnesium bromide or allylmagnesium bromide, respectively, gave complex reaction mixtures in which, together with the expected phenyl- or allyl-transfer products (**11a** and **11b**, respectively), an appreciable amount of **10**, arising from isobutyl transfer, was present (Chart I, runs 1 and 2). Moreover, when the reaction was performed in ether (Chart I, run 3) only **10** was recovered with complete, but "inverted", chemoselectivity!

Scheme I

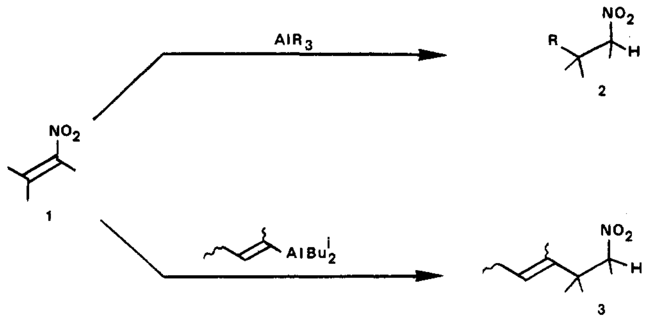
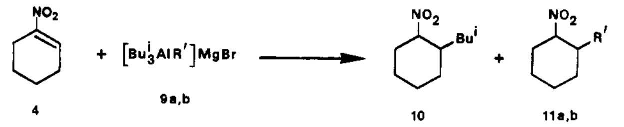


Chart I

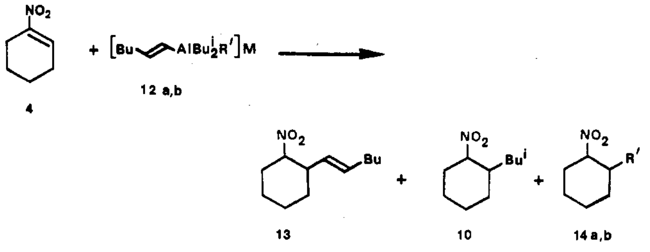


R′ = phenyl (a); allyl (b).

Run	R′	Solvent[a]	Product Distribution (%) 10	11
1	Phenyl	A	65	35
2	Allyl	A	43	57
3	Phenyl	B	100	-

[a] A = 1/3 (v/v) hexane/ether; B = ether

Chart II



R′M = MeMgBr (a); n-BuLi (b).

Run	R′M	Product Distribution % 13	10	14
1	MeMgBr	68	23	9
2	n.BuLi	29	26	45

An unsatisfactory degree of alkenyl transfer was also observed when 4 was reacted in a hexane/ether (4/1 v/v) solvent mixture with trialkylalkenylalanates prepared in situ (see Experimental Section). The chemoselectivity observed in the reaction of such reagents with 4 is strongly

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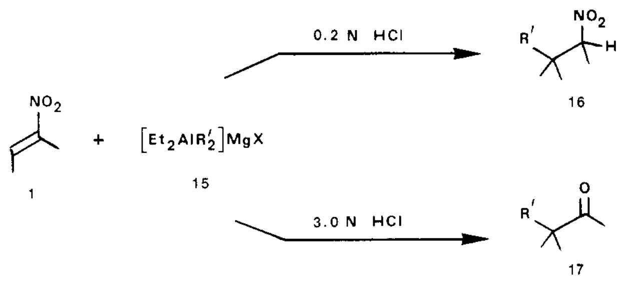
(1) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, *53*, 45.

(2) Pecunioso, A.; Menicagli, R. *Tetrahedron* **1987**, *43*, 5411.

(3) (a) Eisch, J. J. In *Comprehensive Organometallic Chemistry*, 1st ed.; Pergamon: New York, 1982; Vol. 1, p 555. (b) Zietz, J. R., Jr.; Robinson, G. C.; Lindsay, K. L. *Ibid.* Vol. 7, p 365.

0022-3263/89/1954-2391$01.50/0

Scheme II

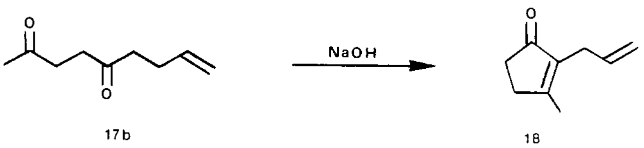


influenced by the nature of the counterion (Mg or Li) (Chart II).

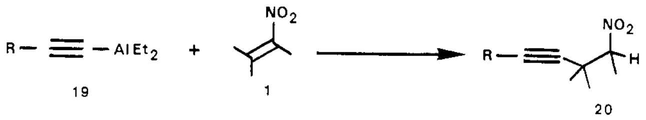
These results were surprising since a wide number of studies have showed that mixed tetraorganoalanates are able to transfer the unsaturated ligand in preference to the saturated ones. In particular, lithium "ate" complexes, such as **12b**, are effective alkenylating agents of carbon dioxide,[3,6] alkyl halides,[3] carbonyl compounds,[3] and α,β-unsaturated ketones.[3,7] To the best of our knowledge only Negishi et al.[8] have reported the occurrence of the preferential alkyl-group transfer in the reaction of trialkylalkenylalanates with *tert*-alkyl halides. To rationalize such results, which could not be explained in terms of a ionic two-electron transfer process, the authors[8] proposed a one-electron transfer mechanism. Since nitro olefins are good electron acceptors, owing to their low-lying LUMO, the product distributions observed in the reactions of 1-nitrocyclohexene with tetraorganoalanates (Chart I and Chart II) do indeed support such an assumption.

The lack of selectivity displayed by $[R_3AlR']M$ prompted us to study the reaction of **1** with $[Et_2AlR'_2]MgX$ (**15**), prepared in situ from Et_2AlCl and 2 molar equiv of the corresponding R'MgX (R' = allyl, benzyl, phenyl; X = Br, Cl). Such organometallic reagents showed very good selectivity leading to the R' transfer products **16** or **17** (Scheme II); only in a few cases were minor amounts (~ 5%) of ethyl transfer products detected by GC–MS analysis (Table I). Compounds **16** and **17** were recovered in good yields (Table I, runs 1–8 and runs 9 and 10, respectively) under suitable hydrolysis conditions (Scheme II, procedure A and B, see Experimental Section). As previously stated,[2] in the reaction of the cyclic systems **4** and **5**,[9] an accurate temperature control is necessary in the hydrolysis step in order to obtain high diastereoisomeric purity. In fact, if the hydrolysis of the reaction mixture is performed in the range 0 °C to room temperature, lower cis/trans ratios of the recovered **16a,b,e,g** are obtained. In contrast with the results obtained by starting from **4** and **5**, no appreciable diastereoselectivity was observed in the reaction of **7**, from which a 1/1 erythro/threo isomeric mixture of **16d** (Table I) was recovered; pure samples of both these diastereoisomers[10] were obtained by flash chromatography.

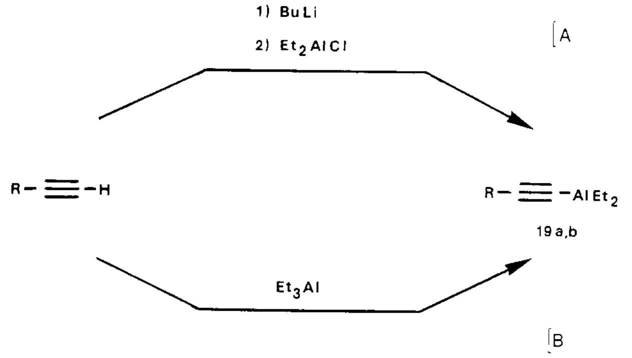
Scheme III



Scheme IV



Scheme V



R = n-Butyl (a) ; Phenyl (b)

The reported process is valuable in organic synthesis largely because the conjugate addition of the allyl group to nitro olefins[11] allows the formation of either δ-nitro olefins or α-allylated ketones[12] in very good yields. These latter compounds are important intermediates,[13] and a wide number of procedures have been devised for their synthesis,[14] but many of the reported protocols suffer from incomplete regiocontrol or require multistep approaches.

We have applied the described allylation procedure to the preparation of the allylrethrone (**18**), a component of insecticidal pyrethroid,[15] which was obtained through the cyclization of diketone **17b** (Scheme III).

Attempts to transfer an alkynyl group to **4** using $[R_2AlR'_2]M$ (R' = 1-hexynyl) failed, even though the organometallic derivatives **15** are able to transfer allyl, benzyl, and phenyl groups to nitro olefins. However, the conjugate alkynylation of nitro olefins was successfully performed by means of ether-free diethylalkynylalanes (**19**), which had been prepared in a hexane solution by adding either alkynyllithium to Et_2AlCl (Scheme IV, procedure a) or the suitable alkyne to $AlEt_3$[16] (Scheme IV,

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[4] (a) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1. (b) Ono, N.; Kaji, A. *Synthesis* **1986**, 693. (c) Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751. (d) Kabalka, G. W.; Gai, Y.; Goudgaon, N. M.; Varma, R. S.; Gooch, E. E. *Organometallics* **1988**, *7*, 493 and references cited therein.

[5] When the reaction of either triisobutylaluminum or diethylallylaluminum with 1-nitrocyclohexene were performed in diethyl ether it was recovered only the unreacted precursor.

[6] Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754.

[7] See also: (a) Floyd, M. B.; Weiss, M. J. *J. Org. Chem.* **1979**, *44*, 71. (b) Bernady, K. F.; Floyd, M. B.; Poletto, J. F.; Weiss, M. J. *Ibid.* **1979**, *44*, 1438 and references cited therein.

[8] Baba, S.; Van Horn, D. E.; Negishi, E. *Tetrahedron Lett.* **1976**, 1927.

[9] For specific studies on the protonation of the nitronate anions see also: (a) Angyal, S. J.; Luttrell, B. M. *Aust. J. Chem.* **1970**, *23*, 1485. (b) Zimmerman, H. E.; Nevins, T. E. *J. Am. Chem. Soc.* **1957**, *79*, 6559. (c) Trager, W. E.; Vincenzi, F. F.; Huitric, A. C. *J. Org. Chem.* **1962**, *27*, 3006.

[10] Configurational assignment were done on the basis of the ^1H NMR upfield shift showed by the signal of the CH_3 group in the erythro isomer, where a gauche conformational arrangement between the CH_3 and the phenyl groups is present. For similar considerations see: Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353 and references cited therein.

[11] Ochiai, M.; Arimoto, M.; Fujita, E. *Tetrahedron Lett.* **1981**, 1115.

[12] Such addition has been previously performed by means of allyltrimethylsilanes in the presence of Lewis acids; the resulting nitronic acid was then threated with aqueous $TiCl_3$ to give the allylated ketones in 48–74% yield (see ref 11).

[13] Cormier, R. A.; Morris, T. E. *Synth. Commun.* **1987**, *17*, 1673 and references cited therein.

[14] Ono, N.; Hamamoto, I.; Kaji, A. *J. Org. Chem.* **1986**, *51*, 2832, and references cited therein.

[15] (a) Liu, Z.; Rong, G. *Synth. Commun.* **1986**, *16*, 871. (b) Ellison, R. A. *Synthesis* **1973**, 397 and references cited therein.

Table I. Reaction of Nitro Olefins 4–8 with $[Et_2AlR'_2]MgX$

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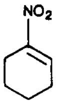
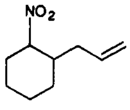
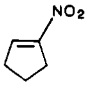
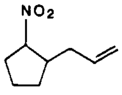
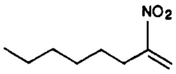
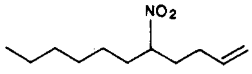
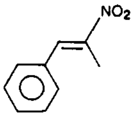
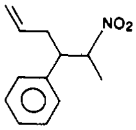
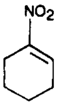
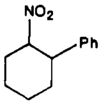
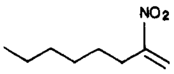
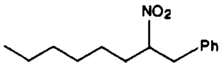
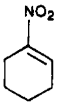
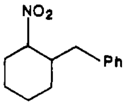
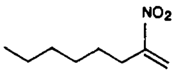
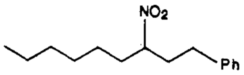
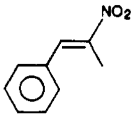
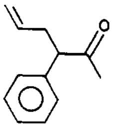
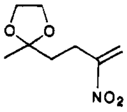
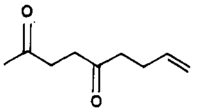
1	 4	allyl	A	 16a	93/7	86[c]
2	 5	allyl	A	 16b	95/5	94
3	 6	allyl	A	 16c	–	93
4	 7	allyl	A	 16d	50/50	91
5	 4	phenyl	A	 16e	100	78[c]
6	 6	phenyl	A	 16f	–	83
7	 4	benzyl	A	 16g	94/6	85
8	 6	benzyl	A	 16h	–	89
9	 7	allyl	B	 17a	–	78
10		allyl	B	 17b	–	86[c]

[a] A = 0.2 N HCl; B = 3.0 N HCl. [b] Determined by GLC and ^1H NMR analyses. [c] Ethyl transfer products (≈5%) were also present in the crude reaction mixture.

procedure b). The reaction of **19a,b** with both **4** and **7** gave the γ-nitroalkynyl derivatives **20** (Scheme V, Table II) along with a minor amount (10–15%) of ethyl transfer products. The diastereoisomeric ratios and the relative configurations of pure samples of **20** were determined as described above for compounds **16**.[17]

These last results are noteworthy since it has been reported that the reaction of **1** when performed with magnesium acetylides furnished the alkynylated nitro olefins **19** in low yield,[18] while titanium acetylides gave only dimerization products.[19]

The spectroscopic characterization of the recovered compounds **16–18** and **20** are presented in Table III.

Conclusion

This paper represents the concluding part of our studies on the reactivity of nitro olefins with organoaluminum compounds and deals with the results obtained in the

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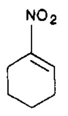
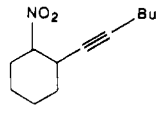
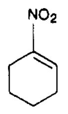
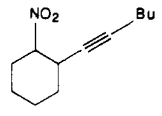
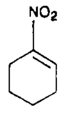
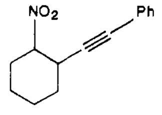
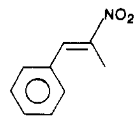
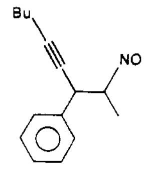
[16] Rienacker, R.; Schwengers, D. *Justus Liebigs Ann. Chem.* **1970**, *737*, 182.

[17] In case of **20c** no pure samples of the erythro and threo isomers were obtained from the flash chromatography. The NMR spectra were therefore recorded on the recovered diastereoisomeric mixture.

[18] Mechkov, T. D.; Sulimov, I. G.; Usik, N. V.; Perekalin, V. V.; Mladenov, I. *Zh. Org. Khim.* **1978**, *14*, 733.

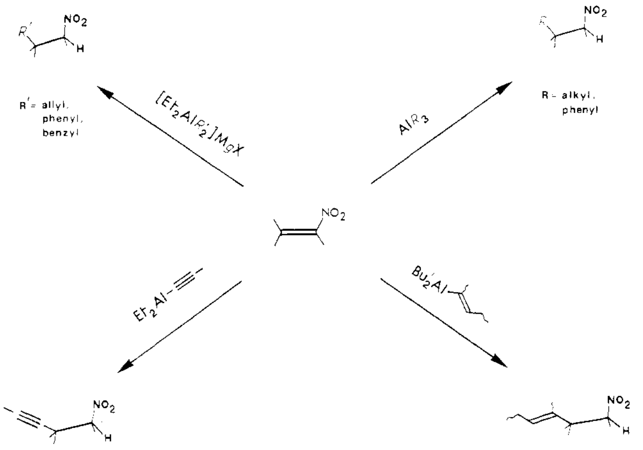
[19] Krause, N.; Seebach, D. *Chem. Ber.* **1987**, *120*, 1845.

Table II. Reaction of Nitro Olefins 4 and 7 with Diethyldiallylalanes

run	nitro olefin	Et_2AlR, R	preparation procedure[a]	product	diastereoisomeric ratio[b]	yield, %
1	 **4**	*n*-BuC≡C–	A	 **20a**	90/10	75
2	 **4**	*n*-BuC≡C–	B	 **20a**	90/10	82
3	 **4**	PhC≡C–	B	 **20b**	100	87
4	 **7**	*n*-BuC≡C–	B	 **20c**	73/27	84

[a] A = alkyne/butyllithium/Et_2AlCl; B = alkyne/$AlEt_3$. [b] Determined by GLC and ^1H NMR analyses.

Scheme VI



reactions of the substrates 1 with tetraorganoalanates and dialkylalkynylalanes. We observed that the reactions of $[R_3AlR']M$ with nitro olefins proceed with an unusually low or even "wrong" chemoselectivity; on the other hand $[Et_2AlR'_2]MgX$ transfers allyl, benzyl, and phenyl groups in a very high selective process. We have showed, moreover, that alkynyl groups can be delivered in the conjugate position of 1 using diethylalkynylalanes.

The present results, along with those previously reported[1,2] (Scheme VI), clearly point out that the reactions of organoaluminum compounds with nitro olefins represent a general and versatile synthetic tool for the preparation of a wide number of functionalized intermediates.[4,20]

Experimental Section

Materials and Instrumentation. All the rections were carried out in dry apparatus under argon. Diisobutylaluminum hydride (DIBAH) and butyllithium were employed in a hexane solution (Aldrich, 1.0 and 1.6 M, respectively). Triethylaluminum, diethylaluminum chloride, and triisobutylaluminum were redistilled and stored in sealed capillary glass vials in weighed amounts. Allylmagnesium bromide, phenylmagnesium bromide, benzylmagnesium chloride, and methylmagnesium bromide were obtained as 0.5–1.5 M solutions in diethyl ether. 1-Nitrocyclohexene (**4**),[21] 1-phenyl-2-nitropropene (**7**),[22] and 4-(2-methyl-1,3-dioxolan-2-yl)-2-nitrobutene (**8**)[23] were prepared as reported. 1-Nitrocyclopentene (**5**) and 2-nitro-1-octene (**6**) were obtained via the experimental procedure reported for similar compounds.[20] Hexane, benzene, and diethyl ether were purified by standard methods and distilled from $LiAlH_4$ before use. GLC analyses were peformed on a Perkin-Elmer 3920B instrument (SE-30, 2 m × 0.29 cm column) equipped with flame ionization detector and using N_2 as the carrier gas. IR spectra (ν cm^{-1}) were obtained on a Perkin-Elmer FT-IR 1750 spectrophotometer using liquid films (20 μm). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 (200 and 50 MHz) spectrometer. All NMR data were obtained in $CDCl_3$ solutions, and chemical shifts (δ ppm) are referred to tetramethylsilane (^1H NMR) or $CDCl_3$ (^{13}C NMR) as internal reference. Mass spectra (*m/z*, relative intensity) were taken on a VG-Analytical 7070 GC–MS instrument. All the isolated **16–18** and **20** gave satisfactory elemental analyses (0.4%). Analytical TLC were performed on silica gel (Merck, SiO_2 60), and the crude products were purified by flash chromatography[24] (Merck, SiO_2 60, 230–400 mesh).

Reaction of 4 with 9a or 9b. An ethereal solution of the appropriate Grignard reagent (6 mmol) was added dropwise to a cooled (0 °C) hexane solution (10 mL) of Al-*i*-Bu_3 (6 mmol). The mixture was stirred at room temperature (1 h) and cooled to −15 °C. Then a solution of 1-nitrocyclohexene (5 mmol) in hexane/ether (1/1 v/v, 20 mL) was added. The resulting suspension was stirred to room temperature (30 min) and then hydrolyzed (procedure A) to give a crude mixture in which **10** and **11** were the main components (GLC). The compounds **10** and **11** were identified by comparison of their GLC retention time and GC–MS spectra with those of authentic samples. Run 2 (Chart I) was performed in ethyl ether.

Reaction of 4 with 12a and 12b. A hexane solution of DIBAH (7 mmol) was added to a cooled (0 °C) solution of 1-hexyne (7 mmol) in the same solvent (15 mL); the resulting colorless solution

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(20) See also: (a) Yoshikoshi, A.; Miyashita, M. *Acc. Chem. Rev.* **1985**, *18*, 284. (b) Rosini, G.; Petrini, M.; Sorrenti, P. *Synthesis* **1985**, 515 and references cited therein. (c) Holzappfel, C. W.; Marais, C. F.; van Dyk, M. S. *Synth. Commun.* **1988**, *18*, 97 and references cited therein.

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Table III. Spectroscopic Data of the Isolated Compounds

compd	mol wt[a]	mass spectra	IR[b]	^{1}H NMR[c,d]	^{13}C NMR[c,d]
16a	169.2 ($C_9H_{15}NO_2$)	139 (2), 123 (10), 107 (15), 93 (24), 81 (100), 67 (61)	1642, 1545, 1377, 996, 917	5.84–5.61 (m, 1), 5.12–4.96 (m, 2), 4.68–4.59 (m, 0.95), 4.25 (dt, *J* = 11.0, 4.1 Hz, 0.05),* 2.53–0.90 (m, 11)	135.51, 117.28, 90.46,* 85.90, 38.69, 29.63, 27.54, 26.64, 22.20, 21.88
16b	155.2 ($C_8H_{13}NO_2$)	109 (14), 93 (30), 79 (27), 67 (100)	1642, 1547, 1375, 996, 919	5.91–5.65 (m, 1), 5.20–4.80 (m, 2 + 0.1*), 4.55 (ddd, *J* = 11.3, 5.4, 2.3 Hz, 0.9), 2.75–1.10 (m, 9)	135.87,* 135.20, 117.27, 116.49,* 90.81, 90.10,* 45.69, 45.61,* 37.67, 33.79,* 31.81, 30.96,* 30.74, 29.56,*, 23.54, 22.38*
16c	199.3 ($C_{11}H_{21}NO_2$)	111 (4), 109 (8), 97 (19), 83 (31), 69 (48), 55 (100)	1643, 1552, 995, 917	5.87–5.65 (m, 1), 5.12–5.00 (m, 2), 4.57–4.42 (m, 1), 2.20–0.90 (m, 17)	136.09, 116.42, 88.09, 33.74, 32.75, 31.30, 29.56, 28.47, 25.55, 22.29, 13.76
16d	205.2 ($C_{12}H_{15}NO_2$)	158 (6), 143 (7), 130 (36), 118 (100), 105 (37), 91 (59)	1642, 1551, 955, 920, 764, 703	7.40–7.10 (m, 5), 5.62–5.38 (m, 1), 5.08–4.87 (m, 2); 4.76 (dq, *J* = 9.6, 6.6 Hz, 1), 3.22 (dt, *J* = 9.6, 5.4 Hz, 1), 2.55–2.30 (m, 2), 1.30 (d, *J* = 6.6 Hz, 3)	138.34, 134.51, 129.02, 128.57, 127.78, 117.66, 87.54, 50.00, 36.88, 17.44
		189 (1), 188 (2), 158 (12), 143 (7), 130 (38), 118 (100), 105 (33), 91 (78)		7.42–7.13 (m, 5), 5.65–5.37 (m, 1), 5.10–4.87 (m, 2), 4.83 (dq, *J* = 9.2, 6.6 Hz, 1), 3.26 (dt, *J* = 9.2, 8.4 Hz, 1), 2.59–2.31 (m, 2), 1.60 (d, *J* = 6.6 Hz, 3)	138.01, 134.66, 128.73, 128.27, 127.67, 117.67, 87.28, 49.69, 34.89, 20.83
16e	205.2 ($C_{12}H_{15}NO_2$)	205 (5), 159 (16), 158 (12), 129 (4), 117 (12), 115 (10), 91 (100)	1545, 1372	7.41–7.14 (m, 5), 4.98–4.89 (m, 1), 3.05 (dt, *J* = 12.0, 4.3 Hz, 1), 2.55–1.60 (m, 8)	140.47, 128.47, 127.30, 127.18, 87.21, 45.22, 30.24, 25.07 (2 C), 20.11
16f	235.3 ($C_{14}H_{21}NO_2$)	189 (23), 188 (17), 117 (28), 104 (43), 91 (100)	1551, 748, 700	7.37–7.10 (m, 5), 4.78–4.62 (m, 1), 3.24 (dd, *J* = 14.2, 8.6 Hz, 1), 3.02 (dd, *J* = 14.2, 5.8 Hz, 1), 2.15–1.65 (m, 2), 1.50–1.15 (m, 8), 0.87 (t, *J* = 6.4 Hz, 3)	135.89, 128.96, 127.49, 90.03, 39.94, 33.38, 31.26, 28.40, 25.53, 22.25, 13.73
16g	219.3 ($C_{13}H_{17}NO_2$)	189 (4), 171 (3), 143 (2), 129 (7), 107 (36), 91 (100)	1543, 1380, 741, 701	7.37–7.10 (m, 5), 4.74–4.45 (m, 1), 2.95–1.15 (m, 11)	139.07, 128.87, 128.34, 126.19, 90.83,* 85.78, 42.41,*, 41.22, 38.97,* 35.86, 32.15,* 29.22,* 27.91, 26.42, 24.66,*, 24.47,* 22.53, 21.96
16h	249.3 ($C_{15}H_{23}NO_2$)	147 (1), 131 (4), 117 (16), 107 (22), 104 (25), 91 (100)	1551, 750, 700	7.40–7.15 (m, 5), 4.56–4.41 (m, 1), 2.70–2.51 (m, 2), 2.43–2.23 (m, 1), 2.08–1.89 (m, 2), 1.84–1.58 (m, 1), 1.45–1.15 (m, 8), 0.95–0.85 (m, 3)	140.42, 129.06, 128.83, 126.86, 88.43, 35.59, 34.08, 32.17, 31.55, 28.71, 25.78, 22.53, 13.99
17a	174.2 ($C_{12}H_{14}O$)	174 (3), 159 (1), 131 (100), 116 (14), 91 (44), 77 (11)	1714	7.45–7.15 (m, 5), 5.85–5.45 (m, 1), 5.12–4.91 (m, 2), 3.70 (t, *J* = 7.5 Hz, 1), 2.55–2.35 (m, 2), 2.05 (s, 3)	207.88, 138.55, 135.90, 129.02, 128.39, 127.46, 116.63, 59.38, 35.98, 16.76
17b	154.2 ($C_9H_{14}O_2$)	154 (4), 111 (17), 99 (100), 96 (32), 83 (36), 71 (31)	1713, 1642, 999, 916	5.91–5.70 (m, 1), 5.10–4.94 (m, 2), 2.81–2.10 (m, 8), 2.19 (s, 3)	208.70, 207.26, 137.06, 115.11, 41.51, 36.60, 35.83, 29.50, 27.41
18	136.2 ($C_9H_{12}O$)	136 (100), 121 (77), 107 (10), 93 (79), 79 (92)	1698, 1646, 1386, 996, 913	5.85–5.68 (m, 1), 5.05–4.93 (m, 2), 3.96 (d, *J* = 6.3 Hz, 2), 2.58–2.50 (m, 2), 2.41–2.35 (m, 2), 2.07 (s, 3)	209.12, 171.53, 138.09, 134.67, 115.08, 33.98, 31.39, 26.88, 16.88
20a	209.3 ($C_{12}H_{19}NO_2$)	162 (9), 147 (7), 133 (5), 119 (8), 105 (10), 97 (39), 91 (28), 79 (36), 67 (71), 55 (100)	2249, 1548	4.60–4.45 (m, 0.9), 4.29 (dt, *J* = 11.0, 4.6 Hz, 0.1),* 3.63–3.53 (m, 1), 2.30–1.10 (m, 14), 0.90 (t, *J* = 6.8 Hz, 3)	89.94,* 85.75, 85.27, 75.94, 32.99, 30.95, 30.78, 25.22, 23.90, 21.85, 20.60, 18.31, 13.54
20b	229.3 ($C_{14}H_{15}NO_2$)	183 (9), 168 (9), 155 (19), 142 (30), 129 (31), 116 (100), 106 (52), 89 (74), 77 (50)	2236, 1546, 1377, 788, 758, 692	7.46–7.23 (m, 5), 4.38 (dq, *J* = 11.0, 4.5 Hz, 1), 3.85–3.75 (m, 1), 2.40–1.20 (m, 8)	131.82, 128.27 (m + p), 122.79, 96.09, 85.63, 85.17, 33.30, 30.42, 25.32, 23.70, 20.58
20c	245.3 ($C_{15}H_{19}NO_2$)	199 (17), 198 (100), 183 (6), 171 (22), 155 (16), 141 (29), 129 (43), 128 (39), 115 (37), 105 (15), 91 (68)	2237, 1551, 759, 702	7.45–7.15 (m, 5), 4.79–4.68 (m, 1), 4.41 (dt, *J* = 7.2, 2.3 Hz, 0.27),* 4.16 (dt, *J* = 8.5, 2.3 Hz, 0.73), 2.29–2.11 (m, 2), 1.72–1.18 (m, 4), 1.60 (d, *J* = 6.7 Hz, 0.81),* 1.37 (d, *J* = 6.7 Hz, 2.19), 0.98–0.3 (m, 3)	137.12,* 136.22, 128.81, 128.47, 128.13*, 127.94, 87.72, 87.33,* 86.08, 76.67, 42.88,* 42.74, 30.59,* 30.53, 21.71,* 21.64, 18.14, 16.48, 15.40,* 13.29

[a] All isolated products gave satisfactory C, H, and N analyses (±0.4%). [b] Liquid film, 20 μm. [c] All spectra were measured in $CDCl_3$; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [d] Marked (*) values are referred to the signals of the minor component.

was heated at 50 °C for 2 h. The mixture was cooled (0 °C) and either methylmagnesium bromide (7 mmol) in ether or butyllithium (7 mmol) in hexane/ether (1/1 v/v, 20 mL) was added dropwise. After stirring at room temperature (1 h), the formed white suspension was cooled to −15 °C, and a solution of 1-nitrocyclohexene (5 mmol) in hexane/ether (10 mL) was added dropwise. The mixture was stirred at room temperature (30 min) and then hydrolyzed according to procedure A. The recovered crude product was analyzed by GLC (Chart II), and the compounds **13**, **10**, and **14** were identified by comparing their GLC retention times and their GC–MS and ^{1}H NMR spectra with those of authentic samples.

Reaction of 4–8 with 15. General Procedure. Twelve millimoles of the appropriate Grignard reagent (Table I), dissolved in 30 mL of ethyl ether, was added to a cooled (0 °C) hexane solution (30 mL) of diethylaluminum chloride (12 mmol). The white suspension was stirred at room temperature (4 h) and cooled to −15 °C. Then a solution of the appropriate nitro olefin (10 mmol) in hexane/ether (1/1 v/v, 25 mL) was added dropwise. The mixture was stirred at room temperature (30 min) and then hydrolyzed according to either procedure A or procedure B. The recovered crude **16** and **17** were purified by flash chromatography[24] using acetone/petroleum ether or ethyl acetate/petroleum ether as eluting mixtures.

Preparation of Allylrethrone 18. According to the reported procedure[25] the diketone **17b** (1.08 g, 7 mmol) was dissolved in 11 mL of ethyl alcohol and reacted with 13 mL of 0.5 N NaOH solution. The resulting mixture was heated at reflux for 5 h and then worked up as usual;[23] from the crude reaction mixture, 0.88

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g (92%) of pure **18** was recovered by flash chromatography[24] (ethyl acetate/petroleum ether, 1/4).

Preparation of 19a and 19b. Procedure A. 1-Hexyne (13 mmol) in hexane (10 mL) was added to a cooled (−15 °C) hexane solution (10 mL) of butyllithium (13 mmol). The formed white suspension was stirred at room temperature (30 min) and cooled to 0 °C. Then a hexane solution (15 mL) of diethylaluminum chloride (13 mmol) was added, and the resulting mixture was stirred for an additional 2 h before use.

Procedure B. Via the reported procedure,[16] the alkyne (15 mmol) was added to 13 mmol of triethylaluminum cooled at 0 °C. The mixture was stirred 48 h at room temperature, and additional alkyne (4 mmol) was added; the resulting solution was heated at 50 °C (15 h) and then diluted with 30 mL of hexane.

Reaction of 4 or 7 with 19. General Procedure. A benzene solution (15 mL) of the nitro olefin (10 mmol) was added dropwise to a cooled (−15 °C) hexane solution of the diethylalkynylalane **19** (13 mmol). The mixture was stirred at room temperature (30 min) and then hydrolyzed according to procedure A. The crude products obtained were purified by flash chromatography[24] (ethyl ether/petroleum ether, 4/96).

Hydrolysis. Procedure A. The cooled (0 °C) reaction mixture was poured into a flask containing 250 mL of a cooled (−10 °C) and vigorously stirred 0.2 N HCl solution saturated with NaCl and ether (50 mL). Sometimes a precipitate is formed from the reaction of the nitro olefins with **15** or **19**. In this case, the solid was triturated, suspended in ether, and added to the acid mixture. The organic product was extracted into ether (3 × 50 mL) and dried over Na_2SO_4. The solvent was evaporated (20 mmHg) to give crude products **16** and **20**, which were in turn purified by flash chromatography.[24]

Procedure B. The reaction mixture was poured into 200 mL of 3.0 N HCl solution and vigorously stirred for 2 h; the organic product was extracted into ether (3 × 50 mL) and dried over Na_2SO_4. The solvent was removed at reduced pressure, and crude products **17a** and **17b** were purified by flash chromatography.[24]

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Registry No. 4, 2562-37-0; **5**, 22987-82-2; **6**, 2783-14-4; **7**, 705-60-2; **8**, 113810-80-3; **10**, 118921-40-7; **11a**, 74221-87-7; **11b**, 118921-39-4; **13**, 118921-41-8; **14a**, 74221-86-6; **14b**, 118921-42-9; *cis*-**16a**, 118921-43-0; *trans*-**16a**, 118921-44-1; *cis*-**16b**, 118921-45-2; *trans*-**16b**, 118921-46-3; **16c**, 118921-47-4; **16d** (isomer 1), 118921-48-5; **16d** (isomer 2), 118921-49-6; **16f**, 118921-50-9; *cis*-**16g**, 118921-51-0; *trans*-**16g**, 118921-52-1; **16h**, 118921-53-2; **17a**, 26965-15-1; **17b**, 5312-86-7; **18**, 3569-36-6; *cis*-**20a**, 118921-54-3; *trans*-**20a**, 118921-55-4; **20b**, 118921-56-5; **20c** (isomer 1), 118921-57-6; **20c** (isomer 2), 118921-58-7; DIBAH, 1191-15-7; Al-*i*-Bu_3, 100-99-2; PHC≡CH, 536-74-3; 1-hexyne, 693-02-7; diethylaluminum chloride, 96-10-6; triethylaluminum, 97-93-8.

Soluble, Graphitic Ribbon Topologies. A Synthetic Strategy and First Model Studies

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A strategy for the synthesis of graphitic, ribbon-shaped polymers is presented which is based on repetitive Diels–Alder (DA) methodology involving bifunctional, partially aromatic dienes and bifunctional dienophiles like benzoquinone. This paper describes related model studies, the results of which are interpreted as good evidence for the feasibility of the outlined strategy. The synthesis of novel, alkyl chain substituted polycyclic aromatic compounds **5**, **6**, **8**, **10b–d**, **11c,d**, and **13** is described. Compounds **10c,d** and **13** show surprisingly high solubilities in chloroform at room temperature. Finally, the structure of the "S"-shaped quinone derivative **11c** as derived from an X-ray analysis is presented.

Introduction

Ribbon-shaped (or ladder) polymers constitute an intriguing and aesthetically pleasing class of structures. For more than 20 years, chemists have focused attention on syntheses of such structures, because of their potential applications as either thermally stable, liquid crystalline, or electrically conducting materials; also, interesting mechanical properties may be anticipated for such materials. Ribbon structures which can be considered as part of the graphite lattice are of special interest, since their properties are expected to lie between those of known ladder polymers and that of graphite. In a survey of the literature, two main problems associated with ribbon syntheses are observed, namely, achieving a regular well-defined structure and proving the structure. Due to the multiple-stranded nature of ladder molecules, their synthesis involves formation of at least two bonds between each adjacent pair of monomer units, a situation prone to generate structural irregularities. Most ribbon-shaped structures, especially those with a high degree of unsaturation, e.g., graphitic ribbons, are rigid species and, hence, more or less insoluble. Consequently, a reliable elucidation of their structures turned out to be rather difficult, in many cases impossible.[1]

Up to now, progress in the synthesis of graphitic ribbons was achieved from two different directions. On the one hand, pyrolytic techniques were developed, converting suitable monomers to ribbons under harsh conditions.[2] Because no measures were taken to solubilize the ribbons obtained, these materials were intractable and the assignment of structure remained uncertain. The second approach was based on a stepwise construction of ribbon precursor topologies under mild conditions. Hart, Miller,

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