(3) Available from Givaudan Corp. as Melonal.
(4) This enyne has been made previously by fragmentation of caranone tosylhydrazone: J. W. Wheeler, R. H. Chung, Y. N. Vaishnav, and C. C. Shroff, *J. Org. Chem.*, **34**, 545 (1969).
(5) W. I. Taylor and A. R. Battersby, "Cyclopentanoid Terpene Derivatives", Marcel Dekker, New York, N.Y., 1969.
(6) F. G. De Las Heras, S. Y-K. Tam, R. S. Klein, and J. J. Fox, *J. Org. Chem.*, **41**, 84 (1976); R. B. Davis and D. H. Scheiber, *J. Am. Chem. Soc.*, **78**, 1675 (1956); CIBA Ltd., Belgian Patent 620 022; *Chem. Abstr.*, **59**, 8840f (1963).
(7) A special class of this reaction, the cyclization of the enols of acetylenic ketones, has been investigated.[11]
(8) R. M. Carlson and A. R. Oyler, *Tetrahedron Lett.*, 2615 (1974); R. M. Carlson, A. R. Oyler, and J. R. Peterson, *J. Org. Chem.*, **40**, 1610 (1975).
(9) W. D. Huntsman et al., *J. Org. Chem.*, **27**, 1983 (1962).
(10) D. Uhrick, Ph.D. Thesis, Ohio University, 1972.
(11) J. M. Conia, *Synthesis*, 1 (1975).
(12) W. D. Huntsman et al., *J. Am. Chem. Soc.*, **80**, 5455 (1958).

trans-1-*N*-Acylamino-1,3-dienes: Preparation from Dienoic Acids

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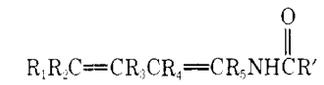
The convenient preparation of *trans* 1-*N*-acylamino-1,3-dienes from conjugated dienoic acids by a modified Curtius procedure is reported. This procedure is specifically illustrated by the preparation of the 1,3-butadiene and 1,3-pentadiene carbamates, thiocarbamates, and ureas (**4–13**) in yields of 44–80%. The ^{13}C NMR spectra of these acylamino-1,3-dienes have been determined, and the shift assignments are discussed.

Dienamides are extremely useful components for Diels–Alder synthesis.[2] The application of *N*-acyl-*N*-alkyl-1-amino-1,3-butadienes for the intramolecular Diels–Alder elaboration of natural products has been impressively demonstrated by Oppolzer and co-workers,[3] while recent reports from our laboratory have clearly demonstrated the utility of *N*-acyl-1-amino-1,3-dienes, and intermolecular Diels–Alder strategies, for solving stereochemical problems in the area of alkaloid total synthesis.[4]

A recent report from our laboratory described a versatile synthetic route to both *N*-trichloroacetyl-1-amino-1,3-dienes (**1**, R′ = CCl_3) and *N*-trichloroacetyl-2-amino-1,3-dienes.[5]



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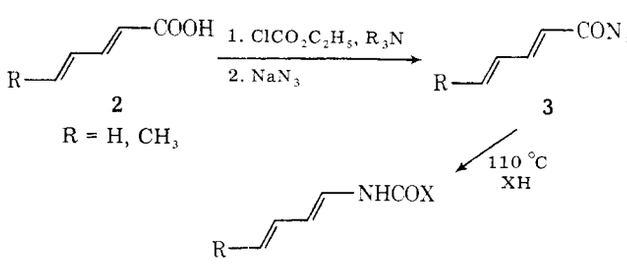
Synthetic applications of these dienes were limited to a certain extent, however, by their moderate Diels–Alder reactivity, a property attributed to the electron-withdrawing nature of the trichloroacetyl substituent. In this paper we report[6] that a variety of *trans*-1-*N*-acylamino-1,3-dienes can be conveniently prepared, on large scales, from dienoic acids using a modified Curtius sequence.[7] This route provides a general entry to the more reactive dienamides **1**[8] which have heteroatom acyl substituents (R′ = OR, SR, NR_2).

Results

Preparation. Dienoic acids **2** were converted, via their mixed anhydrides, into the azide derivatives **3.** The acyl azides were not isolated but instead extracted into toluene and added directly to a refluxing toluene solution containing the free-radical inhibitor 4-*tert*-butylcatechol. The diene isocyanate thus produced was either trapped as it was formed (procedure A) or cooled to room temperature before the trapping agent was added (procedure B). Concentration of the toluene solution and filtration through silica gel afforded the pure crystalline *trans*-1-*N*-acylamino-1,3-dienes **4–13** in overall yields of 44–80%. It is critical that the crude dienamides be purified immediately, as yields were dramatically reduced if the concentrated toluene solution was stored for several days before purification. Results are summarized in Table I.



2
R = H, CH_3

3

4, R = H; X = $OCH_2C_6H_5$
5, R = H; X = $OC(CH_3)_3$
6, R = H; X = OC_2H_5
7, R = H; X = OC_6H_5
8, R = H; X = SC_6H_5
9, R = H; X = $N(CH_2)_4$
10, R = CH_3; X = OC_2H_5
11, R = CH_3; X = OC_6H_5
12, R = CH_3; X = SC_6H_5
13, R = CH_3; X = $N(CH_2)_4$

The in situ trapping procedure (procedure A) is preferred for the preparation of diene carbamates, but it was markedly inferior for the preparation of diene ureas. The latter result is likely due to decomposition of the more reactive diene ureas in refluxing toluene. The amount of trapping reagent used was dictated by its ease of removal from the product dienamide. When a trapping reagent was employed which was not significantly more reactive than ethanol (e.g., *tert*-butyl alcohol or benzyl alcohol), the ethanol produced from the mixed anhydride condensation had to be removed in order to avoid the formation of contaminating amounts of the ethyl carbamate **6.** This is most easily done by concentrating the acyl azide solution to one-half its volume on a rotary evaporator, with ethanol being removed as a toluene azeotrope. In our early experiments we experienced significant problems with reproducibility. After convincing ourselves that this did not derive from the source or purity of the sodium azide employed,[9] we looked in greater detail at the mixed anhydride formation step. In our hands the reaction of *trans*-2,4-pentadienoic acid and ethyl chloroformate was not reproducible using standard conditions.[7] However, this reaction was totally reliable when *N,N*-diisopropylethylamine was substituted for triethylamine as the acid scavenger.

Properties. Dienamides **4–13** are reasonably stable crystalline solids which, when pure, can be stored in a freezer (but not at room temperature) for several months with little decomposition. The only exceptions are the phenyl thiocarbamates **8** and **12,** which decompose in a freezer within days with the loss of thiophenol.

The ^{13}C NMR spectra for the acylamino-1,3-dienes prepared in this study, and for *trans*-1-trichloroacetamido-1,3-butadiene (**14**),[5] are summarized in Table II.[10] For the butadienes the assignment for the terminal methylene carbon

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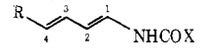
Table I. Preparation of *trans*-1-*N*-Acylamino-1,3-dienes

Dienamide	R	X	Procedure[a] (equiv of HX)	Mp, °C	Isolated yield, %
4	H	$OCH_2C_6H_5$	A (0.8)	74–75	53[b]
			B (0.8)		35[c]
5	H	$OC(CH_3)_3$	A (3)	67–68	59
			B (3)		44
10	CH_3	OCH_2CH_3	A (5)	91–92	80
6	H	OCH_2CH_3	A (5)	44–45	71[b]
11	CH_3	OC_6H_5	A (5)	118–120	72
7	H	OC_6H_5	B (1)[d]	118–119	66
			A (1)		45
13	CH_3	$N(CH_2)_4$	B (1)	164–165	77
			A (1)		10[c]
9	H	$N(CH_2)_4$	B (1)	163–164	44
12	CH_3	SC_6H_5	B (1)	116–118	78
8	H	SC_6H_5	B (1)	92–93	47

[a] Isocyanate was trapped as formed at 110 °C (procedure A), or isocyanate was preformed at 110 °C and trapped at 25 °C (procedure B). The amount of trapping reagent employed is shown in parentheses. [b] Mean yield of four to six preparations. All other table entries are nonoptimized yields of a single experiment. [c] Yield estimated by ^1H NMR spectroscopy. [d] A few drops of triethylamine were added.

Table II. ^{13}C NMR Spectra and Assignments for *trans*-1-*N*-Acylamino-1,3-dienes



Diene	Registry no.	R	X	Chemical shift[a] C_1	C_2	C_3	C_4	Other
4	65899-49-2	H	$OCH_2C_6H_5$	127.2	112.5	134.6	113.5	128.3 (p-C_6H_5), 128.4 and 128.7 (o and m-C_6H_5), 136.0 (ipso C_6H_5), 153.7 (C=O), 67.5 (CH_2)
5	65899-50-5	H	$OC(CH_3)_3$	127.8	111.3	134.9	112.7	28.3 (CH_3), 80.9 ($\mathbf{C}(CH_3)_3$), 152.9 (C=O)
6	61759-61-3	H	OC_2H_5	127.6	112.1	134.8	113.2	14.5 (CH_3), 61.7 (CH_2), 154.1 (C=O)
7	61759-55-5	H	OC_6H_5	126.7	113.5	134.3	114.1	121.6 (o-C_6H_5), 125.8 (p-C_6H_5), 129.5 (m-C_6H_5), 150.8 (ipso C_6H_5),*[5] 151.9 (C=O)*
8	61759-58-8	H	SC_6H_5	125.7	114.3	134.2	115.0	127.5 (ipso C_6H_5), 129.5 (m-C_6H_5), 130.0 (p-C_6H_5), 135.5 (o-C_6H_5), 164.6 (C=O)
9	61759-62-4	H	$N(CH_2)_4$	128.8	110.0	135.5	111.6	25.5 ($\mathbf{C}H_2CH_2N$), 45.8 ($\mathbf{C}H_2N$), 153.4 (C=O)
14	59403-10-9	H	CCl_3	124.4	118.6	133.4	117.3	92.0 (CCl_3), 159.1 (C=O)
10	61759-53-3	CH_3	OCH_2CH_3	124.8*	111.9	128.9	125.4*	14.5 (CH_3), 18.0 (=$\mathbf{C}CH_3$), 61.6 (CH_2), 154.0 (C=O)
11	61759-54-4	CH_3	OC_6H_5	123.9	113.3	128.5	126.4	18.1 (CH_3), 121.6 (o-C_6H_5), 125.7 (p-C_6H_5), 129.4 (m-C_6H_5), 150.7 (ipso C_6H_5),* 152.1 (C=O)*
12	61759-57-7	CH_3	SC_6H_5	123.1	114.2	128.5	127.2	18.2 (CH_3), 127.6 (ipso C_6H_5), 129.4 (m-C_6H_5), 129.7 (p-C_6H_5), 135.4 (o-C_6H_5), 164.3 (C=O)
13	61759-56-6	CH_3	$N(CH_2)_4$	126.0	109.7	129.5	123.6	18.1 (CH_3), 25.4 ($\mathbf{C}H_2CH_2N$), 45.7 (CH_2N), 153.3 (C=O)

[a] In $CDCl_3$; chemical shifts are given in ppm from internal Me_4Si; assignments with an asterisk may be reversed.

can be uniquely made on the basis of off-resonance decoupled spectra. The vinylic carbon resonance at 134.2–135.5 ppm, which is similar to the central carbon of 1,3-butadiene (136.9 ppm), is easily assigned to C_3 since this carbon, like a meta carbon of a substituted benzene, should be only slightly affected by a trans substituent at carbon 1. The observation of this resonance at ca. 135 ppm also confirms the expected trans stereochemistry since C_3 would be shifted noticeably upfield if the substituent at carbon 1 were cis oriented. The carbon absorptions at 124.4–128.8 ppm are assigned to C_1 on the basis of chemical shift additivity relationships using the 11.1-ppm downfield shift (relative to benzene) for the ipso carbon of acetanilide[11] as a model for the butadiene series. The assignments for the acylaminobutadiene vinylic carbons are internally consistent and show the expected effects of changes in the electron-donating ability of the acylamino substituent. Thus, carbons 2 and 4 are observed at progressively higher field for the series **14** (X = CCl_3), **6** (X = OC_2H_5), and **9** (X = $N(CH_2)_4$). This trend of increasing electron density in the butadiene π system is of course also observed in the butadiene vertical ionization potentials (ψ_2) measured by photoelectron spectroscopy: **14**, 8.66 eV; **6**, 8.21 eV; and **9**, 7.90 eV.[8] The ^{13}C shift assignments for the acylaminopentadienes are easily made from a consideration of the expected chemical shift effects of a terminal trans methyl substituent.[12]

Discussion

Only a few examples previously existed of the conversion of a dienoic acid to a 1-*N*-acylamino-1,3-diene. Sorbic acid (*trans,trans*-2,4-hexadienoic acid) was reported to be converted in low yield to a pentadiene urea by a Curtius sequence,[13] and sorbic amide and 4-phenyl-2,4-pentadienamide were reported to be converted under Hoffman conditions to the corresponding methyl carbamates in good yield.[14] The modified Curtius procedure detailed here makes 1,3-diene carbamates, thiocarbamates, and ureas generally available,

on large scales, from dienoic acid precursors. It is particularly noteworthy that this procedure succeeds in the labile butadiene series, and one would expect yields to be even higher in more substituted cases. Since a variety of conjugated dienoic acids are readily accessible from Knoevenagel, Wittig, and related reactions,[15] 1-*N*-acylamino-1,3-dienes with both a diversity of carbon skeletons and acyl substituents should be conveniently available by this method. Diene carbamates promise to be extremely useful components for Diels–Alder synthesis,[4] and it is particularly significant that their preparation from dienoic acids allows one to specifically tailor the acyloxy function (amino-protecting group) for later synthetic manipulation. A recent study of the Diels–Alder reaction of acylaminobutadienes **4–9** has confirmed the expectation of an increase in reactivity with increasing electron-donating ability of the acyl substituent, although the effects observed were not large.[8] With a diversity of 1-*N*-acylamino-1,3-dienes readily available, a variety of synthetic applications await exploration.

Experimental Section[16]

***trans*-2,4-Pentadienoic acid** was prepared by a modification of the original procedure of Doebner.[17] We have found this procedure to give higher yields and to be more convenient than other commonly used procedures for preparing this material.[18] A 1-L three-neck flask was equipped with a mechanical stirrer, an ice water chilled condenser topped with a calcium chloride drying tube, and a dropping funnel. The flask was charged with 210 mL (2.6 mol) of pyridine, vigorous stirring was begun, and 208 g (2.0 mol) of powdered malonic acid was added portionwise. Acrolein (150 mL, 2.2 mol) was then added dropwise over 30 min to the resulting vigorously stirred suspension. An exothermic reaction began immediately with vigorous carbon dioxide evolution and gentle reflux ensued. The reaction was allowed to continue for 1 h, at which time carbon dioxide evolution had nearly ceased. The reaction mixture was then poured into 1 L of ice and carefully acidified with 130 mL of concentrated sulfuric acid. The aqueous mixture was extracted with four 250-mL portions of dichloromethane, and the organic extracts were dried ($MgSO_4$) for about 10 min and filtered. The dichloromethane solution was concentrated to about 300 mL on a rotary evaporator and allowed to crystallize in a refrigerator (−10 °C) for several hours. Filtration afforded a first crop of 40–50 g. Three additional crops were taken after successive concentrations to 150, 70, and 30 mL. After vacuum drying (over P_2O_5), the combined four crops yielded 86–100 g (44–51%) of off-white crystals, mp 69–71 °C. This material appears free of polymer and is satisfactory for the next step. Material of this purity may be stored in a freezer for several months without significant decomposition. Pure *trans*-2,4-pentadienoic acid melts at 72 °C.[17,18]

Modified Curtius Rearrangement: Procedure A (In Situ Trapping). Benzyl *trans*-1,3-Butadiene-1-carbamate (4). A 1-L three-neck flask was fitted with a stirring bar, a thermometer, and a dropping funnel. The flask was flushed with nitrogen and charged with 49 g (0.50 mol) of *trans*-2,4-pentadienoic acid, 80 g (0.62 mol) of *N,N*-diisopropylethylamine, and 300 mL of acetone, and the resulting solution was cooled to 0 °C. A solution of 55 g (0.50 mol) of ethyl chloroformate and 150 mL of acetone was added over 30 min while maintaining the temperature below 0 °C. After stirring for an additional 30 min at 0 °C, a chilled solution of 65 g (1.0 mol) of sodium azide and 150 mL of water was added. The mixture was stirred for an additional 15 min at 0 °C and poured into 500 mL of ice water. The acyl azide was isolated by extraction with six 250-mL portions of toluene, dried over $MgSO_4$ for about 20 min, and filtered, and residual ethanol was removed by concentration to a volume of about 300 mL on a rotary evaporator. The acyl azide solution was then added over 30 min to a vigorously stirred solution of 43 g (0.40 mol) of benzyl alcohol, 250 mg of 4-*tert*-butylcatechol, and 200 mL of dry toluene while rapid reflux was maintained. Reflux was continued for 10–30 min by which time the acyl azide (2130 cm^{-1}) and isocyanate (2270 cm^{-1}) IR bands had disappeared. The reaction mixture was rapidly cooled to room temperature and concentrated to afford a yellow semisolid residue which was purified immediately. Crystallization of this residue from 95% ethanol (50 mL; −25 °C) yielded 39–46 g of pale yellow crystalline product, mp 69–72 °C. Column chromatography (silica gel; 9:1 hexane–ethyl acetate) of the oily residue afforded a second batch of crystalline product, bringing the yield to 50–57 g (49–56%) of nearly pure **4**, mp 70–73 °C. An analytical sample was prepared by recrystallization from hexane–ethyl acetate: mp 74–75 °C; IR ν_{max} (Nujol) 3300, 1692, 1625, 1515, 1230, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (s, C_6H_5), 6.71 (broadened d, J = 9 Hz, =C**H**NH), 6.26 (apparent dt, J = 10, 17 Hz, C**H**=CH_2), 5.4–5.8 (m, C**H**=CHNH and NH), 5.15 (s, $CH_2C_6H_5$), 4.8–5.2 (m, =CH_2); mass spectrum, *m/e* 203.093 (25) ($C_{12}H_{13}NO_2$ requires *m/e* 203.095), 144 (12), 92 (14), 91 (100).

***tert*-Butyl *trans*-1,3-Butadiene-1-carbamate (5).** In a similar reaction which employed *tert*-butyl alcohol (3 equiv) as the trapping agent, 33.3 g (0.34 mol) of *trans*-2,4-pentadienoic acid afforded, after one recrystallization from ethanol–water, 34.1 g (59%) of nearly pure **5**, mp 61–63 °C. An analytical sample was prepared by two recrystallizations from ethanol–water: mp 67–68 °C; IR ν_{max} (Nujol) 3300, 1690, 1620, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.1–7.3 (m, vinylic and NH), 4.5–5.0 (m, =CH_2), 1.47 (s, $C(CH_3)_3$); mass spectrum, *m/e* 169.110 (10) ($C_9H_{15}NO_2$ requires *m/e* 169.110).

In our early experiments the mixed anhydride was prepared using triethylamine (1.1 equiv) as the base and excess ethyl chloroformate (1.3 equiv). (This procedure is *not* recommended.) The toluene solution of the acyl azide was also not concentrated (to remove ethanol), and 1–5 equiv of the trapping reagent was employed. Using these modifications of the procedure described for the preparation of **4**, the following dienes were prepared on a 80–100-mmol scale. In all cases the crude product was purified by chromatography on silica gel (hexane–ether). Yields refer to chromatographically homogeneous crystalline samples.

Ethyl *trans*-1,3-butadiene-1-carbamate (6) was prepared in 60–91% yield (six preparations). Recrystallization from hexane–ether afforded an analytical sample: mp 44–45 °C; IR ν_{max} (Nujol) 3360, 1695, 1665, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7 (broadened d, NH), 5.3–6.9 (m, vinylic), 4.5–5.1 (m, =CH_2), 4.13 (q, J = 7 Hz, OCH_2), 1.26 (t, J = 7 Hz, CH_3); mass spectrum, *m/e* 141.079 (34) ($C_7H_{11}NO_2$ requires *m/e* 141.079), 69 (49), 44 (100), 43 (47).

Phenyl *trans*-1,3-butadiene-1-carbamate (7) was prepared in 45% yield when a few drops of triethylamine were added to catalyze phenol addition to the isocyanate. Recrystallization from hexane–ether afforded an analytical sample: mp 118–119 °C; IR ν_{max} (Nujol) 3310, 1715, 1660, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.2–7.7 (m, C_6H_5, vinylic, and NH), 4.5–5.2 (m, =CH_2); mass spectrum, *m/e* 189.079 (12) ($C_{11}H_{11}NO_2$ requires *m/e* 189.079), 95 (7), 94 (100), 67 (8).

Diene **7** was also obtained in 66% yield when the isocyanate was preformed (procedure B).

Ethyl *trans,trans*-1,3-pentadiene-1-carbamate (10) was prepared from sorbic acid in 80% yield. Recrystallization from dichloromethane afforded an analytical sample: mp 91–92 °C; IR ν_{max} (Nujol) 3300, 1705, 1670, 1640, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–7.0 (m, vinylic), 4.15 (q, J = 7 Hz, CH_2O), 1.67 (d, J = 6 Hz, =CCH_3), 1.23 (t, J = 7 Hz, CH_2CH_3); mass spectrum, *m/e* 155 (26), 82 (100), 67 (32), 55 (37). Anal. ($C_8H_{13}NO_2$): C, H, N.

Phenyl *trans,trans*-1,3-pentadiene-1-carbamate (11) was prepared from sorbic acid in 72% yield: mp 118–120 °C; IR ν_{max} (Nujol) 3260, 1735, 1705, 1660, 1640, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–7.7 (m, C_6H_5, vinylic, and NH), 1.68 (d, J = 6 Hz, =CCH_3); mass spectrum, *m/e* 203.095 (6) ($C_{12}H_{13}NO_2$ requires *m/e* 203.095), 112 (12), 97 (12), 94 (100).

Procedure B (Preformed Isocyanate). *N*-(*trans,trans*-1,3-Pentadien-1-yl)-1-pyrrolidinecarboxamide (13). A solution of 11.9 g (0.11 mol) of ethyl chloroformate and 40 mL of acetone was added dropwise to a stirred solution of 9.52 g (85 mmol) of sorbic acid (*trans,trans*-2,4-hexadienoic acid), 10.2 g (0.10 mol) of triethylamine, and 50 mL of acetone at 0 °C. (This procedure for making the mixed anhydride is *not* recommended.) After 30 min a solution of 8.45 g (0.13 mol) of sodium azide and 30 mL of water was added dropwise while maintaining the temperature below 10 °C. After 1 h the reaction mixture was poured into 200 mL of ice water and extracted with three 60 mL-portions of toluene, and the toluene solution was dried over $MgSO_4$ for 30 min. The acyl azide solution was then added dropwise over 1 h to 100 mL of refluxing toluene which contained ca. 50 mg of 4-*tert*-butylcatechol. Reflux was continued for 30–60 min, by which time the acyl azide IR band (2130 cm^{-1}) had disappeared, and the reaction mixture was rapidly cooled to room temperature by placing it in an ice–water bath. A solution of 7.1 mL (85 mmol) of freshly distilled pyrrolidine and 30 mL of xylene was added over 30 min, by which time IR analysis indicated that the isocyanate band (2270 cm^{-1}) had disappeared. The reaction mixture was concentrated to afford a brown solid, which was purified by column chromatography (silica gel, ethyl acetate) to afford 11.8 g (77%) of **13** as a white solid, mp 163–164 °C. Recrystallization from hexane–ethyl acetate afforded an analytical sample: mp 164–165 °C; IR ν_{max} (Nujol) 3310, 1658, 1650, 1630, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–7.4 (m, vinylic and NH), 3.1–3.5 (m, NCH_2), 1.7–2.1 (m, NCH_2CH_2), 1.70 (d, J = 6 Hz,

=CCH_3); mass spectrum, *m/e* 180.129 (57) ($C_{10}H_{16}N_2O$ requires *m/e* 180.126), 114 (26), 98 (100), 55 (57).

***N*-(*trans*-1,3-Butadien-1-yl)-1-pyrrolidinecarboxamide (9)** was prepared in a similar fashion in 44% yield. Recrystallization from hexane–ethyl acetate afforded an analytical sample: mp 163–164 °C; IR ν_{max} (Nujol) 3250, 1671, 1630, 1600, 1510 cm^{-1}; ^1H NMR ($CDCl_3$), δ 5.2–7.5 (m, vinylic and NH), 4.5–4.9 (m, $=CH_2$), 3.0–3.5 (m, NCH_2), 1.5–1.9 (m, NCH_2CH_2); mass spectrum, *m/e* 166.109 (30) ($C_9H_{14}N_2O$ requires *m/e* 166.111), 98 (100), 55 (85).

Phenyl *trans,trans*-1,3-pentadiene-1-thiocarbamate (12) was prepared in a similar fashion in 78% yield. This diene was labile and showed considerable decomposition, with the formation of thiophenol, when stored for 1 week at −20 °C. Recrystallization from ether–hexane afforded an analytical sample: mp 116–118 °C; IR ν_{max} (Nujol) 3220, 1660, 1630, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ (5.0–7.8 (m, C_6H_5, vinylic, and NH), 1.64 (d, J = 6 Hz, $=CCH_3$); mass spectrum, *m/e* 219.070 (17) ($C_{12}H_{13}NOS$ required *m/e* 219.072), 110 (100) (C_6H_5SH probably formed from decomposition), 109 (56), 81(20), 80 (19).

Phenyl *trans*-1,3-butadiene-1-thiocarbamate (8) was prepared in a similar fashion in 47% yield. This diene was labile and showed considerable decomposition, with the formation of thiophenol, when stored for 1 week at −20 °C. Recrystallization from ether–hexane afforded an analytical sample: mp 92–93 °C; IR ν_{max} (Nujol) 3240, 1645, 1610, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.2–8.0 (m, C_6H_5, vinylic, and NH), 4.5–5.1 (m, $=CH_2$); mass spectrum, *m/e* 205.056 (15) ($C_{11}H_{11}NOS$ requires *m/e* 205.056), 110 (100) (C_6H_5SH probably formed from decomposition), 109 (44), 95 (32).

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Registry No.—**2** (R = H), 21651-12-7; **2** (R = Me), 110-44-1; **3** (R = H), 65899-51-6; **3** (R = Me), 65899-52-7; malonic acid, 141-82-2; *trans*-1-isocyanatobuta-1,3-diene, 65899-53-8; *trans,trans*-1-isocyanatopenta-1,3-diene, 65899-54-9.

References and Notes

(1) A. P. Sloan Foundation Fellow, 1975–1977; Camille and Henry Dreyfus Teacher-Scholar Award Recipient, 1976–1981.
(2) The use of heteroatom-substituted dienes in Diels–Alder reactions has been recently reviewed: S. Danishefsky and L. E. Overman, manuscript in preparation.
(3) W. Oppolzer and W. Fröstl, *Helv. Chim. Acta*, **58**, 587, 590 (1975); W. Oppolzer, W. Fröstl, and H. P. Weber, *ibid.*, **58**, 593 (1975); W. Oppolzer and E. Flaskamp, *ibid.*, **60**, 204 (1977); W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977).
(4) L. E. Overman and P. J. Jessup, *Tetrahedron Lett.*, 1253 (1977); L. E. Overman, L. A. Clizbe, P. J. Jessup, G. F. Taylor, and S. Tsuboi, lecture (L.E.O.) at the 5th International Symposium on Synthesis in Organic Chemistry, Oxford, England, July, 1977; L. E. Overman and P. J. Jessup, *J. Am. Chem. Soc.*, in press.
(5) L. E. Overman and L. A. Clizbe, *J. Am. Chem. Soc.*, **98**, 2352, 8295 (1976).
(6) A preliminary account of this study has been published: L. E. Overman, G. F. Taylor, and P. J. Jessup, *Tetrahedron Lett.*, 3089 (1976).
(7) J. Wienstock, *J. Org. Chem.*, **26**, 3511 (1961).
(8) A quantitative study of the Diels–Alder reaction of a series of *trans*-1-*N*-acylamino-1,3-butadienes and methyl acrylate has been reported: L. E. Overman, G. F. Taylor, K. N. Houk, and L. N. Domelsmith, *J. Am. Chem. Soc.*, in press.
(9) Cf. P. A. S. Smith, *Org. React.*, **3**, 337 (1946).
(10) For other ^{13}C NMR studies of acyclic dienes, see J. W. de Haan and L. J. M. Van de Ven, *Org. Magn. Reson.*, **5**, 147 (1973); O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972); R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963).
(11) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).
(12) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971); P. A. Couperus, A. D. H. Clague, and J. P. C. M. Van Dongen, *Org. Magn. Reson.*, **8**, 426 (1976).
(13) F. Tanimoto, T. Tanaka, H. Kitano, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **39**, 1922 (1966).
(14) V. B. Mochalin, I. S. Varpakhovskaya, and O. P. Beletskaya, *J. Org. Chem. USSR (Engl. Transl.)*, **10**, 1556 (1974).
(15) H. von Barchel and U. Bahr, *Methoden Org. Chem. (Houben Weyl), 4th Ed., 1970*, **5**, Part 1c, 519–555 (1970).
(16) Triethylamine and *N,N*-diisopropylethylamine were purified by distillation from sodium hydride, and acrolein was purified by distillation from anhydrous calcium sulfate. Reagent grade acetone was stored over 4A molecular sieves for at least 24 h before use. 4-*tert*-Butylcatechol was purified by sublimation (50 °C, 0.1 Torr) and recrystallization from hexane. ^1H NMR spectra were determined with a Varian EM 360 or Brucker WH-90 spectrometer. ^{13}C NMR spectra were determined at 22.62 MHz with a Brucker WH-90 spectrometer. ^1H NMR shifts are reported as δ valves in ppm relative to internal Me_4Si. Coupling constants (J) are reported in Hz, and they refer to apparent multiplicities and not true coupling constants; abbreviations used are: s, singlet; d, doublet, t, triplet; m, complex multiplet. Infrared spectra were determined with a Perkin-Elmer Model 283 spectrophotometer. Mass spectra were determined with a DuPont 21-498 B double focusing spectrometer at the Caltech Analytical Facility. Combustion analyses were not obtained on dienes **5–13** since they decomposed slightly (TLC analysis showed material at R_f 0) at room temperature within a few days.
(17) O. Doebner, *Ber.*, **33**, 2140 (1900).
(18) E. P. Kohler and F. R. Butler, *J. Am. Chem. Soc.*, **48**, 1036 (1926); I. E. Muskat, B. C. Becker and J. S. Lowenstein, *ibid.*, **52**, 326 (1930); K. Alder and W. Vogt, *Justus Liebigs Ann. Chem.*, **570**, 196 (1950).

Chloromethylation of Ortho-Disubstituted Benzenes. A Simple Preparation of Some Useful α Isomers of Indan, Tetralin, and Benzosuberane

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Functionalization of ortho-disubstituted benzenes by the chloromethylation procedure has been shown to yield more of the so-called "α isomer" than previously anticipated. The chloromethyl functionality is readily modified to the corresponding alcohol or aldehyde. The aldehyde can be oxidized to the carboxylic acid or reacted with malonic acid (Doebner) to give acrylic acid derivatives. These high-yield manipulations, combined with key purification techniques, have permitted the synthesis of some novel "α-substituted" derivatives of indan, tetralin, and benzosuberane.

We required preparative amounts of indan, tetralin, and benzosuberane derivatives which were substituted on the benzene ring next to the carbocyclic ring, i.e., **1**, **3**, or **5**, the so-called α isomers, and which were capable of being elaborated to derivatives containing functionalized alkyl chains of varying length. However, in contrast to reasonably facile preparations of **2**,[2] **4**,[3] or **6**,[4] i.e., the β isomers, no direct or general methods have been reported for obtaining preparatively useful quantities of isomerically pure α isomers.[5] In general most aromatic substitution reactions of ortho-disubstituted benzenes give a preponderance of the β isomer although some specific conditions of nitration or halogenation have been reported to give mixtures rich in the α isomer.[6]

Thus, the tetralin derivative **3e** has been prepared by a long sequence beginning with the corresponding nitro derivative obtained by fractional distillation[7] or from partially hydro-

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