Conversion of Triphenylamine and Acylated Triphenylamines into 9,10-Diaryl-9-acridanols

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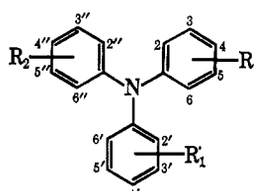
Reaction of triphenylamine with an aromatic carboxylic acid in polyphosphoric acid (PPA) gave 9-aryl-10-phenyl-9-acridanol (**2**) in yields as high as 50%, together with a mixture of *para*-acylated triphenylamines; acridanol **2** arises by cyclization of an intermediate *ortho*-acylated triphenylamine. Certain *para*-monoacylated triphenylamines were rearranged in PPA at 190° into the corresponding acridanols **2** in ~50% yield; *p*-di- and -tribenzoyltriphenylamines under similar conditions gave nuclear-substituted acridanols. The intermolecularity of the above transformations is supported. Acylation of triphenylamine with acid anhydrides and acid chlorides in the presence of anhydrous stannic chloride proceeded readily in benzene solution and provided *para*-acylated triphenylamines.

The Friedel–Crafts and other electrophilic substitution reactions of triphenylamine have been recently studied.[1–4] A consideration of the findings that the products were *para*-substituted derivatives led Baker, *et al.*,[4] to conclude that the *ortho* positions in triphenylamine were sterically hindered. However, a preliminary account[1] of the formation of 9,10-diphenyl-9-acridanol (**2a**) from triphenylamine and benzoic acid in polyphosphoric acid (PPA) indicated otherwise. This synthesis has now been developed and extended to provide a convenient new route to the little-known acridanols **2**, in which *ortho* acylation of triphenylamine features prominently.

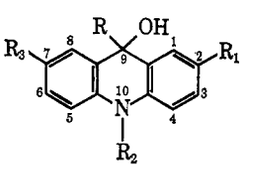
From equimolar amounts of triphenylamine and an aromatic acid in PPA at 120–125° for 0.5 hr, under which conditions rearrangement of *para*-acylated triphenylamines into acridanols did not occur (see below), the corresponding 9-aryl-10-phenyl-9-acridanol (**2**), essentially free of ketone impurity, was afforded in about 10% yield (Table I). The acid-soluble products were formulated as acridanol **2** on the basis of their properties, analysis, and infrared spectra; in several instances the assigned structures were confirmed by comparison with authentic material prepared from N-phenylacridone and the appropriate arylmagnesium bromide.[5]

Compensating for the poor yields of acridanol in the direct synthesis were the advantages of rapidity and apparent general applicability of the method, and the ease of isolation of the product, as compared with the procedure[5] utilizing Grignard reagents. However, not all aromatic acids were successfully employed in the new method, and 4-nitrobenzoic acid, for example, failed to yield acridanol. Glacial acetic acid gave a trace of what may have been the corresponding acridanol, but the reaction with aliphatic acids was not generally examined.

The direct synthesis, which resembles Popp's modification of the Bernthsen acridine reaction[6] with triphenylamine in place of diphenylamine, undoubtedly involves preliminary formation of 2-acyltriphenylamine as an intermediate. That such an *ortho* acylation is sterically feasible was demonstrated by forming 2,7-dimethyl-9-phenyl-10-(*p*-tolyl)-9-acridanol (**2m**) in nearly quantitative yield from 4,4′,4″-tritolylamine (**1h**) and benzoic acid in PPA. In support of the suggested intermediate, 2-benzoyltriphenylamine (**1a**) underwent facile and quantitative conversion into **2a** in PPA at 120°; this cyclization was effected also by anhydrous aluminum chloride, anhydrous stannic chloride, boron trifluoride etherate, and concentrated sulfuric acid.



1a, R = 2-C_6H_5CO; $R_1 = R_2 = H$
b, R = 3-C_6H_5CO; $R_1 = R_2 = H$
c, R = 4-C_6H_5CO; $R_1 = R_2 = H$
d, R = 2-C_6H_5CO; R_1 = 4′-C_6H_5CO; $R_2 = H$
e, R = 4-C_6H_5CO; R_1 = 4′-C_6H_5CO; $R_2 = H$
f, R = 2-C_6H_5CO; R_1 = 4′-C_6H_5CO; R_2 = 4″-C_6H_5CO
g, R = 4-C_6H_5CO; R_1 = 4′-C_6H_5CO; R_2 = 4″-C_6H_5CO
h, R = 4-CH_3; R_1 = 4′-CH_3; R_2 = 4″-CH_3
i, R = 2-C_6H_5CO; R_1 = 4′-CH_3; R_2 = 4″-CH_3
j, R = 3-C_6H_5CO; R_1 = 4′-CH_3; R_2 = 4″-CH_3
k, R = 4-*p*-$CH_3C_6H_4CO$; $R_1 = R_2 = H$
l, R = 4-*p*-$CH_3C_6H_4CO$; R_1 = 4′-*p*-$CH_3C_6H_4CO$; $R_2 = H$
m, R = 4-CH_3CO; $R_1 = R_2 = H$
n, R = 4-*n*-$C_5H_{11}CO$; $R_1 = R_2 = H$



2a, R = $R_2 = C_6H_5$; $R_1 = R_3 = H$
b, R = *o*-$CH_3C_6H_4$; $R_1 = R_3 = H$; $R_2 = C_6H_5$
c, R = *m*-$CH_3C_6H_4$; $R_1 = R_3 = H$; $R_2 = C_6H_5$
d, R = *p*-$CH_3C_6H_4$; $R_1 = R_3 = H$; $R_2 = C_6H_5$
e, R = *o*-BrC_6H_4; $R_1 = R_3 = H$; $R_2 = C_6H_5$
f, R = *m*-BrC_6H_4; $R_1 = R_3 = H$; $R_2 = C_6H_5$
g, R = *p*-BrC_6H_4; $R_1 = R_3 = H$; $R_2 = C_6H_5$
h, R = *o*-IC_6H_4; $R_1 = R_3 = H$; $R_2 = C_6H_5$
i, R = *p*-FC_6H_4; $R_1 = R_3 = H$; $R_2 = C_6H_5$
j, R = C_6H_5; $R_1 = R_3 = H$; R_2 = *p*-$C_6H_5COC_6H_4$
k, R = C_6H_5; $R_1 = C_6H_5CO$; R_2 = *p*-$C_6H_5COC_6H_4$; $R_3 = H$
l, R = C_6H_5; $R_1 = CH_3$; R_2 = *p*-$CH_3C_6H_4$; $R_3 = H$
m, R = C_6H_5; $R_1 = R_3 = CH_3$; R_2 = *p*-$CH_3C_6H_4$
n, R = *p*-$CH_3C_6H_4$; $R_1 = R_3 = H$; R_2 = *p*-$CH_3C_6H_4COC_6H_4$

In addition to acridanol **2a**, the acylation of triphenylamine with benzoic acid afforded an acid-insoluble mixture of unreacted triphenylamine, 4-benzoyltriphenylamine (**1c**), 4,4′-dibenzoyltriphenylamine (**1e**), and 4,4′,4″-tribenzoyltriphenylamine (**1g**); each acyl derivative was identified unequivocally by comparison with authentic material prepared by an appropriate

(1) B. Staskun, *J. Org. Chem.*, **29**, 2856 (1964).
(2) C. J. Fox and A. L. Johnson, *ibid.*, **29**, 3536 (1964).
(3) C. J. Fox and A. L. Johnson, *Makromol. Chem.*, **82**, 53 (1965).
(4) T. N. Baker, W. P. Doherty, W. S. Kelly, W. Newmeyer, J. E. Rogers, R. E. Spalding, and R. I. Walter, *J. Org. Chem.*, **30**, 3714 (1965).
(5) L. H. Cone, *J. Amer. Chem. Soc.*, **36**, 2101 (1914).
(6) F. D. Popp, *J. Org. Chem.*, **27**, 2658 (1962).

TABLE I

DIRECT SYNTHESIS OF SUBSTITUTED 9-ACRIDANOLS (2) FROM TRIPHENYLAMINE (1.2 g, 0.005 mol)

Aromatic acid	Weight of aromatic acid, g	Molar ratio[a]	Reacn temp, °C	Method[b]	Acridanol product	Yield, %[c]	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Benzoic	0.3	1:0.5	120–125	A		12[d,e]								
	0.6	1:1	120–125	A		12[d]								
	1.2	1:2	120–125	A		17[d]								
	2.4	1:4	120–125	A		17[d]	175–177[f]							
	0.3	1:0.5	155–160	A	**2a**[g]	34[d,e]								
	0.6	1:1	155–160	A		15–25[h]		$C_{26}H_{19}NO$	85.93	5.48	4.01	86.00	5.62	3.89
	0.6	1:1	155–160	B		23[d]								
	0.3	1:0.5	190–195	A		48[d,e]								
	0.6	1:1	190–195	A		25–35[h]								
	0.6	1:1	190–195	B		47[d]								
2-Toluic	0.35	1:0.5	160	A		35[d,e]								
	0.7	1:1	155–160	A	**2b**[g]	14[h]	191–192	$C_{26}H_{21}NO$	85.92	5.82	3.85	85.80	5.70	3.58
	0.7	1:1	160	B		28[d]								
3-Toluic	0.7	1:1	190	B	**2c**[g]	38[d]	143–144	$C_{26}H_{21}NO$	85.92	5.82	3.85	85.90	5.75	3.75
4-Toluic	0.7	1:1	120–125	A		10[d]								
	0.7	1:1	155–160	A	**2d**[g]	25[g]	174–176	$C_{26}H_{21}NO$	85.92	5.82	3.85	85.81	5.91	3.75
	0.35	1:0.5	190	A		48[d,e]								
	0.7	1:1	190	B		45–50[d]								
2-Bromobenzoic	1.0	1:1	160	A		12[d]								
	1.0	1:1	195	A	**2e**	26[d]	187–189	$C_{26}H_{18}BrNO$	70.10	4.23	3.27	70.30	4.23	3.38
	1.0	1:1	190	B		22[d]								
3-Bromobenzoic	1.0	1:1	195	B	**2f**	23[d]	*i*	$C_{26}H_{18}BrNO$						
4-Bromobenzoic	1.0	1:1	120–125	A	**2g**	7[d]	197–199	$C_{26}H_{18}BrNO$	70.10	4.23	3.27	70.11	4.23	3.34
	1.0	1:1	190	B		19[d]								
2-Iodobenzoic	1.2	1:1	190	B	**2h**	9[d]	200–203	$C_{26}H_{18}INO$	63.17	3.82	2.95	63.15	3.94	2.87
4-Fluorobenzoic	0.7	1:1	120–125	A		10[d]								
	0.7	1:1	190–195	A	**2i**	15[h]	176–179	$C_{26}H_{18}FNO$	81.72	4.94	3.81	81.33	4.96	3.69
	0.7	1:1	190	B		21[d]								

[a] Triphenylamine/aromatic acid. [b] Method A, reactants were stirred together in PPA (10 g) for 0.5 hr. Method B, aromatic acid was added portionwise over 0.25 hr to a solution of amine in PPA and stirring was continued for an additional 0.25 hr. [c] Crude acridanol. [d] Negligible ketone impurity present. [e] Yield based on aromatic acid. [f] Lit.[5] mp 178°. [g] Structure established by comparison with product of Cone[5] synthesis. [h] Product contaminated with acylated acridanol; purification proved troublesome and required a number of recrystallizations. [i] Acridanol not purified.

TABLE II

SUBSTITUTED TRIPHENYLAMINES (1) PREPARED BY ULLMANN REACTION

Reactants[a] (weight, g)	Yield, %[b]	Product	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Diphenylamine (1[c]), 2-iodobenzophenone (1.5)	40	**1a**	127–128	$C_{25}H_{19}NO$	85.93	5.48	4.01	85.87	5.42	4.11
Diphenylamine (1[c]), 3-iodobenzophenone (1.5)	40	**1b**	139–140	$C_{25}H_{19}NO$	85.93	5.48	4.01	85.82	5.54	4.29
Diphenylamine (1[c]), 4-iodobenzophenone (1.5)	60	**1c**	127–128	$C_{25}H_{19}NO$	85.93	5.48	4.01	85.74	5.69	4.20
4,4′-Dibenzoyldiphenylamine (0.3), iodobenzene (0.7[c])	50	**1e**	143–144	$C_{32}H_{23}NO_2$	(81.50	5.34	2.97)[d]	81.83	5.40	3.31
4,4′-Dibenzoyldiphenylamine (1.2), 2-iodobenzophenone (1.5[c])	70	**1f**	150–151	$C_{39}H_{27}NO_3$	84.00	4.88	2.51	84.07	4.91	2.61
4,4′-Dibenzoyldiphenylamine (0.8), 4-iodobenzophenone (1.5[c])	50	**1g**	176–177[e]	$C_{39}H_{27}NO_3$	84.00	4.88	2.51	83.98	4.83	2.69
4,4′-Ditolylamine (1), 4-iodotoluene (1.1)	20	**1h**	115–116[f]	$C_{21}H_{21}N$	87.76	7.37	4.87	87.84	7.41	4.82
4,4′-Ditolylamine (1), 2-iodobenzophenone (1.5)	50	**1i**	140	$C_{27}H_{23}NO$	85.91	6.14	3.71	85.66	6.15	3.88
4,4′-Ditolylamine (1), 3-iodobenzophenone (1.5)	50	**1j**	105–107	$C_{27}H_{23}NO$	85.91	6.14	3.71	85.89	6.20	3.51
Aniline (5[c]), 4-iodobenzophenone (1.5)	30	*g*	148–149	$C_{19}H_{15}NO$	83.49	5.53	5.13	83.51	5.58	5.22

[a] Amine, iodo compound. [b] Pure compound; recrystallizations from aqueous acetone. The crude yields are not maximal and improvements may well be possible. All the products were obtained as yellow crystals, except 4-benzoyltriphenylamine (**1c**, colorless) and 4,4′,4″-tritolylamine (**1h**, buff). [c] Excess of reactant. [d] Calcd for $C_{32}H_{23}NO_2 \cdot H_2O$. Compound **1e** crystallized from aqueous acetone as the monohydrate, mp 143–144°, as was indicated by analysis and by the (weak) absorption at 2.70 and 2.77 μ in the infrared spectrum. [e] Lit.[2] mp 173.5–175.5°. [f] H. Wieland [*Ber.*, **40**, 4279 (1907)] reports mp 117°. [g] 4-Benzoyldiphenylamine.

Ullmann[7] reaction (Table II). The composition of the acid-insoluble product varied with the molar ratio of reactants employed. Thus, with benzoic acid in large excess (4:1), 4,4′,4″-tribenzoyltriphenylamine (**1g**), was obtained in 80% yield [together with **2a** in improved and apparently maximal yield (17%)]; this is a much more convenient preparation of **1g** than that from benzoyl chloride and aluminum chloride.[2]

When the synthesis of acridanol **2a** from equimolar amounts of reactants was conducted at 160 and 190°, the yield of acid-soluble product was increased, but this now showed (weak–medium) carbonyl absorption in the infrared and was, as found subsequently, contaminated with C-acylated acridanol. Certain other aromatic acids, however, furnished the acridanol **2** virtually free of ketone impurity, even at these elevated reaction temperatures (Table I).

That the C-acylated acridanols were not derived by nuclear acylation of acridanol **2** was shown by recovering acridanol **2a** unchanged after treatment with benzoic acid in PPA at 190°. Their presence became explicable when it was found that certain of the *para*-acylated triphenylamines could be transformed by PPA into acylated acridanols.

A variety of pure acylated triphenylamines were treated with PPA at 190–195° for 0.5 hr with the following results; other observations pertaining to a mechanism are included.

(7) F. Ullmann, *Ber.*, **36**, 2382 (1903).

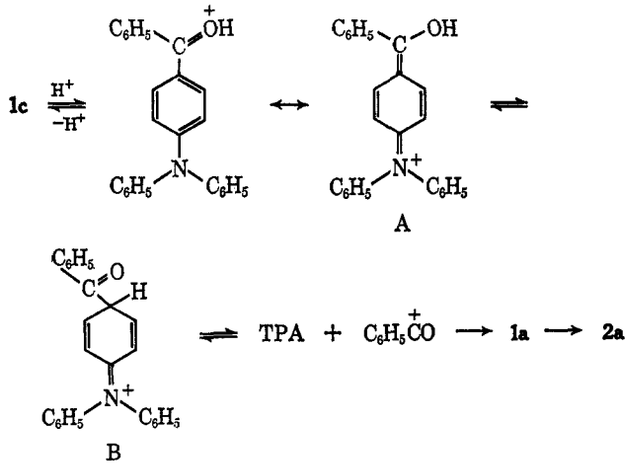
4-Benzoyltriphenylamine (**1c**), although unaffected at 120–125°, was rearranged at the higher reaction temperature into 9,10-diphenyl-9-acridanol (**2a**) in 45% yield; also formed was triphenylamine and other material of unknown constitution. 4-(*p*-Toluoyl)triphenylamine (**1k**) likewise afforded 9-(*p*-tolyl)-10-phenyl-9-acridanol (**2d**) in 55% yield. It was of preparative and mechanistic significance that the acridanols derived in this manner were contaminated with minor amounts only of ketone impurity. In support of an intermolecular process, reaction **1c** → **2a** when conducted in the presence of 4,4′,4″-tritolylamine (**1h**) gave acridanol **2a** together with 2,7-dimethyl-9-phenyl-10-(*p*-tolyl)-9-acridanol (**2m**).

Nuclear-acylated acridanols were obtained on subjecting *p*-di-and triacylated triphenylamines to the action of PPA at 190–195° for 0.5 hr. Thus, 4,4′-dibenzoyltriphenylamine (**1e**) was converted (50%) into a mixture of acridanol **2a** and 10-(*p*-benzoylphenyl)-9-phenyl-9-acridanol (**2j**); benzoic acid sublimed during reaction; its presence was indicative of an intermolecular process. The acid was liberated also when 4,4′,4″-tribenzoyltriphenylamine (**1g**) was transformed (40%) into acridanol **2j** and 2-benzoyl-10-(*p*-benzoylphenyl)-9-phenyl-9-acridanol (**2k**). The products **2j** and **2k** were identified by comparison with samples derived by cyclization of the appropriate 2-benzoyltriphenylamine in PPA or concentrated sulfuric acid. In this respect, the reaction of 2,4′,4″-tribenzoyltriphenylamine (**1f**), to give acridanol **2k**, which involved electrophilic attack on a deactivated nucleus, was noticeably slow compared with that of 2-benzoyltriphenylamine (**1a**) under similar conditions.

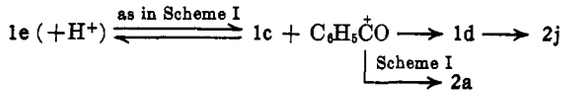
Although the acyl groups in 4,4′,4″-tribenzoyltriphenylamine (**1g**) were not sterically hindered, the compound nevertheless suffered extensive deacylation in PPA at 190° (*cf.* Balaban, *et al.*[8]) as was demonstrated by heating in the presence of excess triphenylamine to give 9,10-diphenyl-9-acridanol (**2a**) as the sole acid-soluble product of reaction.

The above observations and results may be rationalized in terms of the tentative intermolecular processes assumed to occur at 190–195° and depicted in Schemes I (**1c** → **2a**), II (**1e** → **2a** + **2j**), and III (**1g** → **2j** + **2k**).

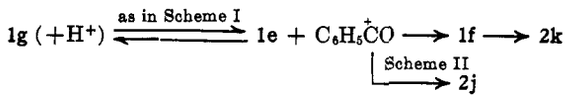
SCHEME I



SCHEME II



SCHEME III

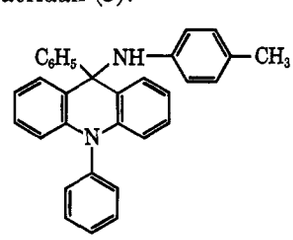


4-Benzoyltriphenylamine (**1c**) and benzoic acid in PPA at 120–125°, however, gave the *para*-acylated derivatives **1e** and **1g**, and negligible acridanol **2j** (and thus **1d**); competitive *ortho* acylation is inhibited presumably because of the proximity to the reaction site of the positively polarized N atom. The production of acridanol **2j** *via* **1c** as in Scheme II may become feasible at 190° if **1c** is less extensively protonated at the higher temperature.

It is noteworthy that the *meta*-acylated bases, *viz.*, 3-benzoyltriphenylamine (**1b**) and 3-benzoyl-4′,4″-dimethyltriphenylamine (**1j**), failed to rearrange into acridanols in PPA at 190–195; in this respect it is significant that these substances are incapable of providing structural contributions analogous to A and B (Scheme I).

In the light of the behavior of the various *para*-acylated triphenylamines in PPA, a modified procedure for acylating triphenylamine with aromatic acids was adopted and led to improved yields (10–50%, depending on the nature of the aromatic acid) of acridanol **2** practically free of ketone impurity (Table I). Thus, addition portionwise, of benzoic acid to a solution of an equimolar amount of triphenylamine in PPA at 190–195°, gave acridanol **2a** in 47% yield. A similar improvement was achieved more conveniently by mixing the amine and benzoic acid in the molar ratio 2:1 and heating with PPA. In these reactions triphenylamine, the least deactivated and hence most reactive substrate competing for acylium ion, RCO^+, was present in excess throughout, with the result that those processes giving rise to C-acylated acridanols (Schemes II and III) were effectively curtailed; moreover, the yield of product was augmented by rearrangement of 4-benzoyltriphenylamine (**1c**) under the reaction conditions prevailing.

When treated with 4-toluidine in PPA acridanol **2a** was converted into what appeared to be 9,10-diphenyl-9-*p*-tolylaminoacridan (**3**).



3

The facility with which triphenylamine undergoes electrophilic substitution has been noted.[1,2,4] It is possible in fact to acylate the amine with acid anhydrides and acid chlorides using benzene as the solvent. Refluxing a benzene solution of equimolar amounts of triphenylamine and benzoic anhydride (or benzoyl chloride) and excess anhydrous stannic chloride for 1 hr, for

(8) M. Frangopol, A. Genunche, N. Negoita, P. T. Frangopol, and A. T. Balaban, *Tetrahedron*, **23**, 841 (1967).

TABLE III

ACYLATION OF TRIPHENYLAMINE (1.2 g, 0.005 mol) IN BENZENE SOLVENT (15 ml)

Acylating agent	Lewis acid	Molar ratio of reactants[a]	Reaction products[b] (yield, %)[c]
Benzoyl chloride	Anhydrous stannic chloride	1:1.05:4	TPA[d] (~15), **1c** (70), **1e** (<5), **1g** (negligible)
		1:2.4:8	TPA (negligible), **1c** (small), **1e** (~40), **1g** (~25)
4-Toluoyl chloride		1:1:4	TPA (25), **1k**[e] (65)
Benzoic anhydride		1:1.1:8	TPA (5), **1c** (69), **1e** (6), **1g** (<5), **2a** (<5)
		1:3.3:12	TPA (negligible), **1c** (negligible), **1e** (~50), **1g** (~20)
n-Hexanoic anhydride		1:1.1:4	**1n**[f] (60)
Acetic anhydride		1:1.1:4	**1m**[g] (65)
Benzoyl chloride	Anhydrous aluminum chloride		
		1:1:2.7	TPA (~40), **1c** (~15), **1e** (~15)
		1:4:4.5	TPA (~10), **1c** + **1e** (small), **1g** (65–70)
4-Toluoyl chloride		1:2.2:2.5	TPA (negligible), **1k** (~3), **1l**[h] (>30)

[a] Triphenylamine/acylating agent/Lewis acid. [b] Separated on a silica gel column; identity confirmed by comparison with Ullmann product (Table II). [c] Crude yield reported, based on triphenylamine. [d] Triphenylamine. [e] Pale yellow crystals from aqueous acetone, mp 92–93°. *Anal.* Calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85. Found: C, 85.63; H, 5.72; N, 3.76. [f] Colorless, viscous gum, bp 200–209 (0.1 mm) [lit.[2] bp 230–235° (0.5 mm)]. *Anal.* Calcd for $C_{24}H_{25}NO$: C, 83.92; H, 7.34; N, 4.08. Found: C, 84.05; H, 7.32; N, 4.03. [g] Colorless crystals from aqueous acetone, mp 143–144° (lit.[2] mp 142–143°). [h] Yellow crystals from aqueous acetone, mp 205–206°. *Anal.* Calcd for $C_{34}H_{27}NO_2$: C, 84.79; H, 5.65; N, 2.91. Found: C, 84.47; H, 5.70; N, 2.91.

example, afforded 4-benzoyltriphenylamine (**1c**) in 70% yield. This method was likewise successful for other *para*-monoacylated triphenylamines (Table III). Utilization of an excess of benzoyl chloride in the presence of anhydrous aluminum chloride under similar conditions, led to 4,4′,4″-tribenzoyltriphenylamine (**1g**) in ~70% yield. Products containing a high proportion of *para*-diacylated triphenylamine resulted from use of other molar proportions of reactants (Table III).

Experimental Section[9]

Direct Synthesis of 9-Aryl-10-phenyl-9-acridanols (2) from Triphenylamine and Aromatic Acids (Table I). General Procedure.—Equimolar amounts of triphenylamine (1.2 g, 0.005 mol) and aromatic acid were stirred together with PPA (10 g, Riedel-de Haën) at 120–125° for 0.5 hr. After cooling and addition of water (~50 ml), acid-insoluble material A was removed, and the (charcoaled) filtrate made alkaline with 5 *N* sodium hydroxide to deposit acridanol **2** (7–12%; negligible carbonyl absorption at 6.0–6.05 μ in the infrared), which was purified by reprecipitation from dilute hydrochloric acid and subsequent recrystallization from either aqueous acetone, aqueous pyridine, or petroleum ether (bp 80–100°). A mixture of **2** and nuclear-acylated acridanol resulted from reaction at 160 or 190° (Table I).

Improved yields of acridanol **2**, likewise virtually free of ketone impurity, were afforded (i) by stirring triphenylamine (1.2 g) and aromatic acid in the molar ratio 2:1, with PPA (10 g) at 190–195° for 0.5 hr, and also (ii) by adding the aromatic acid portionwise over a period of 0.25 hr to a stirred solution of an equimolar amount of triphenylamine (1.2 g) in PPA (10 g) at 190–195° and continuing the heating for an additional 0.25 hr.

Details of the synthesis performed under a variety of conditions as well as other relevant data are given in Table I.

The acridanols **2** dissolved readily in dilute mineral acids and in dilute acetic acid and formed green solutions which exhibited a striking "Flourescein"-like fluorescence in ordinary light. The infrared spectra of the acridanols **2** (listed in Table I) and compounds **2l** and **2m** were very similar in the 2.7–8.6-μ region and all showed sharp peaks at or near 2.80 (m) (OH stretching), 6.20 (s) (medium peak in **2m**), 6.60 (m), 6.70 (s), 6.85 (s), 7.40 (s), 7.60 (m), 7.80 (m–s), 8.60 (m), and 9.7–9.8 (s) μ. The mass spectra of the acridanols **2** (**2a**, **c**, and **m**) all showed a parent peak M, and peaks at M − OH, M − R, and (M − OH − R + 1).

Examination (tlc[9]) of the acid-insoluble material A above, derived from benzoic acid, showed it to contain triphenylamine, 4-benzoyltriphenylamine (**1c**), 4,4′-dibenzoyltriphenylamine (**1e**), 4,4′,4″-tribenzoyltriphenylamine (**1g**), and other (uncharacterized) compounds. When acid-insoluble A (1.4 g) was dissolved in a minimal amount of benzene and chromatographed on silica gel (30 g) with benzene as the eluent, it afforded triphenylamine (fraction 1, purple fluorescence[9]), 0.48 g (40% recovery); compound **1c** (fraction 2, blue fluorescence), 0.30 g (~17%); compound **1e** (fraction 3, blue-purple fluorescence), 0.30 g (~15%); and compound **1g** (fraction 4, blue-purple fluorescence), 0.10 (~4%). The latter (base **1g**) could be readily eluted from the column by means of benzene–acetone (20:1).

With increase of benzoic acid in the acylation the content of di- and triacylated derivatives **1e** and **1g** in the acid-insoluble product A was enhanced at the expense of triphenylamine and compound **1c**. Treatment of triphenylamine (1.2 g) with a 4 *M* proportion of benzoic acid (2.4 g) in PPA (10 g) at 120–125° for 0.5 hr, gave, in addition to acridanol **2a** (0.30 g, 17%), crude 4,4′,4″-tribenzoyltriphenylamine (**1g**, 2.3 g, 80%) contaminated (tlc) by a small amount of compound **1e** and free of triphenylamine and base **1c**.

2,7-Dimethyl-9-phenyl-10-(*p*-tolyl)-9-acridanol (2m) was prepared by stirring 4,4′,4″-tritolylamine (**1h**, 0.25 g) with excess benzoic acid (0.15 g) in PPA (5 g) at 110–130° for 0.5 hr. After addition of water, the mixture was filtered, and the green fluorescent solution was made alkaline to deposit acridanol **2m** (0.30 g, ~90%). Recrystallization of this from aqueous acetone gave colorless crystals, mp 149–150°.

Anal. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.74; H, 6.49; N, 3.53.

9,10-Diphenyl-9-(*p*-tolylamino)acridan (3).—Acridanol **2a** (0.2 g) was reacted with an excess of 4-toluidine (0.2 g) in PPA (4 g) at 120–125° for 0.5 hr. Addition of water afforded a yellow-green fluorescent solution; this was filtered from negligible insoluble impurity and made alkaline to deposit crude **3** contaminated with 4-toluidine. Recrystallization from aqueous acetone gave colorless crystals, mp 199–201°, soluble in dilute mineral acid affording a green fluorescent solution.

Anal. Calcd for $C_{32}H_{26}N_2$: C, 87.63; H, 5.98; N, 6.39. Found: C, 87.05; H, 5.92; N, 6.14.

The infrared spectrum of **3** revealed acridanol **2a** to be absent and displayed a weak absorption at 2.95 (NH stretching) and a medium peak at 12.2 μ (*para* substitution).

Preparation of Substituted Triphenylamines by the Ullmann Reaction (Table II).—The general procedure is illustrated for 2-benzoyltriphenylamine (**1a**). A mixture of diphenylamine (1 g, excess), 2-iodobenzophenone (1.5 g), anhydrous potassium carbonate (0.8 g), and copper powder (50 mg) in nitrobenzene (10 ml) was refluxed for 5–6 hr. After removal of the solvent by steam distillation, the insoluble residue was extracted with benzene and the dried, concentrated extract was chromatographed on silica gel (40 g) using benzene as the eluent. A

(9) Melting points are uncorrected. Infrared spectra consistent with the proposed structures were obtained for all new compounds and were recorded on a Perkin-Elmer Infracord Model 137 spectrophotometer using a 1-mg sample per 300 mg of potassium bromide. Mass spectra were determined from an AEI Model MS-9 mass spectrometer (70 eV). Thin layer chromatography (tlc) was carried out with silica gel G; the mobile phase was benzene containing 1% acetone, and spots were located by visual inspection and/or by their fluorescence in ultraviolet light (350 mμ). Column chromatography was performed with silica gel (Kieselgel, Merck; 0.05–0.20 mm) used without pretreatment; the progress of the separations was followed in ultraviolet light (350 mμ).

fraction with a strong yellow fluorescence[9] was evaporated to afford crude **1a**, recrystallized as yellow crystals from aqueous acetone, mp 127–128°.

Details of the various acylations are collected in Table II.

4,4′-Dibenzoyldiphenylamine.—Ullmann reaction of 4-iodobenzophenone (1.5 g) with 4-aminobenzophenone (1.2 g, excess) as above gave, after removal of nitrobenzene solvent, a dark brown insoluble product. This was extracted successively with 2 *N* hydrochloric acid and with methanol to remove undesirable material, and the residue of 4,4′-dibenzoyldiphenylamine (1 g, ~54%) was recrystallized from 90% (v/v) acetic acid; the pale green crystals, mp 241–242°, were identical (mixture melting point and infrared spectrum) with those from the acylation of diphenylamine with benzoic acid in PPA.[1]

Acylation of Triphenylamine in Benzene Solution (Table III).—The following preparation illustrates the general procedure. A solution of triphenylamine (1.2 g, 0.005 mol) and benzoic anhydride (1.25 g, 0.0055 mol) in benzene (15 ml) was treated with anhydrous stannic chloride (10.5 g, 0.04 mol) and refluxed for 1 hr during which period hydrogen chloride was evolved and some crystalline material separated. Water and benzene were added and a substance B, sparingly soluble in both the aqueous and organic phases, was filtered off. The benzene layer (~50 ml) was washed with 2 *N* sodium hydroxide and water, dried (anhydrous magnesium sulfate), concentrated (rotary evaporator), and chromatographed[9] on silica gel (30 g) using benzene as the eluent to afford the following products (crude yield): triphenylamine (0.06 g, 5%), **1c** (1.2 g, 69%), **1e** (0.14 g, 6%), and **1g** (<0.1 g).

Product B above appeared to be a complex of acridanol **2a** and $SnCl_4$ (or H_2SnCl_6) (see below) and dissolvedg radually on warming with 1 *N* hydrochloric acid; addition of alkali to the green fluorescent solution gave acridanol **2a** (0.06 g, 4%) identified by its infrared spectrum.

Other acid anhydrides and also acid chlorides were treated similarly with triphenylamine in the presence of anhydrous stannic chloride or anhydrous aluminum chloride, and the relevant details and results are shown in Table III.

Formation of 9-Acridanols by Cyclization of 2-Benzoyltriphenylamines. 9,10-Diphenyl-9-acridanol (2a).—The crude product, obtained in methods A–E below, was in each case identified as acridanol **2a** by its infrared spectrum.

A.—2-Benzoyltriphenylamine (**1a**, 0.2 g) dissolved readily in concentrated sulfuric acid (1.5 ml) with an exothermic effect, and a green fluorescent solution was obtained instantly. After remaining at ~20° for 0.5 hr, this was poured into water and the solution made alkaline to deposit crude acridanol **2a** in quantitative yield (0.2 g).

B.—Compound **1a** (0.3 g) and anhydrous aluminum chloride (0.4 g) were intimately mixed and heated at ~120°; a vigorous reaction set in with evolution of hydrogen chloride and yellow fumes. The temperature was kept at 120–140° for 5 min, warm 1 *N* acid HCl was added, and the filtered solution made alkaline to furnish acridanol **2a** in quantitative yield (0.29 g).

C.—2-Benzoyltriphenylamine (**1a**, 0.1 g) was stirred with PPA (2 g) at 110–120° for 20 min. The mixture was treated with water and the solution was basified to give acridanol **2a** (0.09 g, ~90%). When conducted at 20° for 0.5 hr, the reaction led to acridanol **2a** in ~20% yield.

D.—Addition of boron trifluoride etherate (2 ml) to amine **1a** (0.2 g) resulted in a green fluorescent solution. After 0.5 hr, this was treated with water which caused a yellow solid to deposit. The ether was evaporated and the insoluble material (suspected of being a complex of acridanol **2a** and HBF_4 or BF_3) was warmed with hot 2 *N* hydrochloric acid until dissolved; basification of the solution yielded acridanol **2a** (0.18 g, ~90%). A similar sparingly soluble complex was precipitated on addition of an aqueous solution of $NaBF_4$ to a solution of acridanol **2a** in 2 *N* hydrochloric acid.

E.—A solution of amine **1a** (0.1 g) in anhydrous stannic chloride (2 ml, excess) after remaining at ~20° for 1 hr was poured into 1 *N* hydrochloric acid to afford a yellow fluorescent mixture with much insoluble material. The latter was filtered off and warmed with 1 *N* hydrochloric acid when it dissolved; basification of the solution gave acridanol **2a** (~50%). A similar complex was deposited on mixing together 1 *N* hydrochloric acid solutions of acridanol **2a** and stannic chloride.

2-Methyl-9-phenyl-10-(*p*-tolyl)-9-acridanol (2l).—2-Benzoyl-4′,4″-dimethyltriphenylamine (**1i**, 0.5 g) dissolved readily in concentrated sulfuric acid (4 ml) with an exothermic effect. After 0.25 hr at ~20°, water was added and the green fluorescent solution basified to give crude **2l** (0.48 g, ~95%) which was recrystallized as colorless crystals from aqueous acetone, mp 139–140°.

Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 86.04; H, 6.16; N, 3.74.

Formation of 9-Acridanols by Rearrangement of 4-Acylated Triphenylamines. 9,10-Diphenyl-9-acridanol (2a).—4-Benzoyltriphenylamine (**1c**, 1.0 g) was stirred with PPA (10 g) at 190–195° for 0.5 hr and the mixture was treated with water. Acid-insoluble material C (0.5 g) was removed, and the green fluorescent filtrate was made alkaline to deposit acridanol **2a** (0.45 g, 45%; negligible carbonyl absorption) identified by its infrared spectrum. Product C was a mixture (tlc) of triphenylamine, trace amounts of bases **1c** and **1e**, and other substances (unidentified). The conversion into **2a** was less (15–20%) at 155–160°, and negligible at 120–125°.

10-Phenyl-9-(*p*-tolyl)-9-acridanol (2d) was formed (0.38 g, 55%) virtually free of ketone impurity, from 4-*p*-toluoyltriphenylamine (**1k**, 0.7 g) and PPA (7 g) at 190–195° for 0.5 hr, and was identical (infrared spectrum) with acridanol **2d** derived from *p*-tolylmagnesium bromide and N-phenylacridone.

Under similar conditions 3-benzoyltriphenylamine (**1b**) and 3-benzoyl-4′,4″-dimethyltriphenylamine (**1j**) were each converted into an acid- and alkali-insoluble solid which showed weak carbonyl absorption in the infrared spectrum. A trace of suspected acridanol was formed from **1j** (as evidenced by the green fluorescence of the acid reaction solution).

4-Acetyltriphenylamine (**1m**) decomposed to an acid- and alkali-insoluble charcoal-like product; treatment with PPA at 140° for 0.5 hr afforded much unchanged **1m** and a trace of acridanol. An excess of anhydrous aluminum chloride (0.5 g) acting on 4-benzoyltriphenylamine (**1c**, 0.5 g) at 190° for 0.5 hr failed to yield acridanol **2a**; the acid-insoluble product (0.45 g) obtained after addition of water was a mixture (tlc) of triphenylamine, base **1c** (and perhaps **1e**), and other material (unidentified).

Equimolar amounts of amine **1c** (0.35 g) and benzoic acid (0.12 g) in PPA (4 g) were stirred at 120–125° for 0.5 hr. Addition of water afforded an acid-insoluble mixture (tlc) of compounds **1e** and **1g**, while the green fluorescent filtrate contained negligible base.

Intermolecularity of the Amine 1c → Acridanol 2a Rearrangement.—A mixture of 4-benzoyltriphenylamine (**1c**, 0.1 g) and 4,4′,4″-tritolylamine (**1h**, 0.05 g) in PPA (2 g) reacted at 195–200° for 0.5 hr to furnish ~50 mg of acid-soluble base. This was found (infrared and mass spectra) to consist of acridanol **2a** together with 2,7-dimethyl-9-phenyl-10-(*p*-tolyl)-9-acridanol (**2m**).

Formation of Acylated Acridanols by Rearrangement of Di- and Triacylated Triphenylamines. 10-(*p*-Benzoylphenyl)-9-phenyl-9-acridanol (2j).—4,4′-Dibenzoyltriphenylamine (**1e**, 0.8 g, free of mono- and tribenzoyltriphenylamine impurity by tlc) was stirred with PPA (15 g) at 190–195° for 0.5 hr, during which period a trace of benzoic acid (identified by its infrared spectrum) sublimed. After cooling and addition of water, insoluble material D (0.4 g; tlc showed negligible base **1e** present) was removed, and the filtrate was made alkaline to afford a buff-colored product (0.3 g) composed (infrared and mass spectra) of acridanols **2a** and **2j**. The solution of product D in glacial acetic acid (5 ml) was diluted with 1 *N* hydrochloric acid, the mixture was filtered hot (charcoal), and the green fluorescent filtrate was made alkaline to deposit crude **2j**. This was purified by reprecipitation from its (charcoaled) benzene solution with petroleum ether (bp 80–100°) and proved to be indentical (infrared spectrum) with acridanol **2j** prepared as follows. The Ullmann reaction of 4-benzoyldiphenylamine (0.05 g, Table II) with 2-iodobenzophenone (0.2 g, excess) as before gave, after removal of nitrobenzene, crude 2,4′-dibenzoyltriphenylamine (**1d**) which was warmed (90°) with concentrated sulfuric acid (1 ml) for 0.5 hr. Addition of water and filtration of the hot (charcoaled) mixture gave a green fluorescent solution, from which was obtained acridanol **2j** characterized by spectral analysis. Infrared absorption was at 2.85 (m) (OH stretching) and 6.0 μ (s) (CO stretching), and the spectrum which was similar to that of acridanol **2k** (see below) could be distinguished from the latter by comparison of the relative intensities of the respective absorptions at 6.85, 7.4–7.8, 13.0, and 13.85 μ. The mass spectrum (70 eV) showed a weak parent peak at *m/e* 453, a medium peak at *m/e* 436 (M − OH), a medium peak at *m/e* 376 (M − C_6H_5), and a base peak at *m/e* 360 (M − OH − C_6H_5 + 1).

2-Benzoyl-10-(*p*-benzoylphenyl)-9-phenyl-9-acridanol (2k).—4,4′,4″-Tribenzoyltriphenylamine [1g, free (tlc) of mono- and dibenzoytriphenylamine impurity] was stirred with PPA (20 g) at 190–195° for 0.5 hr; a small amount of benzoic acid (identified by its infrared spectrum) sublimed. After cooling, water (~50 ml) was added, acid-insoluble material E (0.6–0.7 g, tlc showed negligible base 1g) was removed, and the filtrate was made alkaline to deposit a pale yellow solid (0.2 g) shown by its infrared and mass spectra to be a mixture of acridanols 2j and 2k. Product E was dissolved in glacial acetic acid (5 ml) and treated as for D above to provide crude acridanol 2k (0.2 g) which was purified by dissolving in benzene and adding petroleum ether (bp 80–100°) to afford a buff-colored solid, mp 115–120°.

Anal. Calcd for $C_{39}H_{27}NO_3 \cdot H_2O$: C, 81.37; H, 5.08; N, 2.43. Found: C, 81.70; H, 5.31; N, 2.46.

The mass spectrum showed a very weak parent peak at *m/e* 557, a weak peak at *m/e* 540 (M − OH), a weak peak at *m/e* 481 (M − C_6H_5 +1), a weak peak at *m/e* 464 (M − OH − C_6H_5 + 1), a base peak at *m/e* 436 (M − OH − C_6H_5CO + 1), and a medium peak at *m/e* 360 (M − OH − $C_6H_5COC_6H_4$ + 1).

A sample of acridanol 2k was prepared unambiguously by cyclization of 2,4′,4″-tribenzoyltriphenylamine (1f, 0.15 g) with PPA (5 g) at 120–125° for 0.5 hr. Addition of water (~100 ml) to the orange fluorescent solution gave a sparingly soluble gum which was separated by decantation and dissolved in glacial acetic acid (5 ml). The acid solutions were combined, warmed to dissolve the sparingly soluble acridanol 2k, filtered hot (charcoal), and made alkaline to afford crude 2k (0.18, ~70%) which was identical (infrared and mass spectra) with the rearrangement product of 1g. In concentrated sulfuric acid (1 ml) conversion of amine 1f (0.2 g) into acridanol 2k proceeded very slowly at 20° compared with the conversion amines 1c and 1i; reaction at 90° for 1 hr afforded base 2k in ~20% yield.

Deacylation of 4,4′,4″-Tribenzoyltriphenylamine (1g).—A mixture of the amine (1g, 0.3 g) and excess of triphenylamine (1 g) in PPA (10 g) was stirred at 190° for 0.5 hr. After addition of water and removal of acid-insoluble material, the green fluorescent filtrate was made alkaline to give 9,10-diphenyl-9-acridanol (2a, 0.25 g, 45% yield, based on complete deacylation of amine 1g) which showed no carbonyl absorption in its infrared spectrum.

Registry No.—1a, 16911-31-2; 1b, 16911-32-3; 1c, 16911-33-4; 1e, 16911-34-5; 1f, 16911-35-6; 1g, 1183-66-0; 1h, 1159-53-1; 1i, 16959-98-1; 1j, 16959-99-2; 4-benzoyldiphenylamine, 4058-17-7; 2a, 16911-37-8; 2b, 16911-38-9; 2c, 16911-39-0; 2d, 16911-40-3; 2e, 16960-00-2; 2f, 16960-01-3; 2g, 16911-41-4; 2h, 16911-42-5; 2i, 16911-43-6; 2j, 16911-44-7; 2k, 16911-45-8; 2l, 16911-46-9; 2m, 16911-47-0; 3, 16911-48-1; triphenylamine, 603-34-9.

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The Reaction of Chlorosulfonyl Isocyanate with Allenes and Olefins[1-3]

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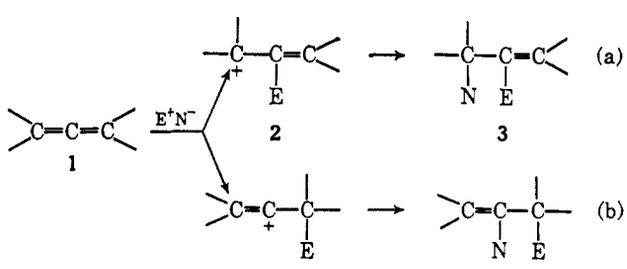
The addition of chlorosulfonyl isocyanate to allenes (2,4-dimethyl-2,3-pentadiene, 2-methyl-2,3-pentadiene, 2,3-pentadiene, 3-methyl-1,2-butadiene, pentamethyleneallene, 1,3-diphenylpropadiene, phenylpropadiene, and cyclononadiene) has been studied. In all cases, initial electrophilic attack occurred at the central carbon atom of the allenic system to produce, in the transition state, an allyl-type stabilized carbonium ion. Structures of the N-chlorosulfonyl-β-lactam cycloadducts and/or 2-carboxamido-1,3-butadiene products have been established on the basis of nmr spectroscopy and conversion into authentic derivatives prepared independently by the reaction of chlorosulfonyl isocyanate with the appropriate olefin. In the case of 3-methyl-1,2-butadiene, a third product identified by degradation and synthesis as 1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea was obtained. Chlorosulfonyl isocyanate added stereospecifically to *cis*- and *trans*-β-methylstyrene to lead to the *cis*- and *trans*-β-lactam, respectively, hydrolysis of which led to *erythro*- and *threo*-3-amino-2-methyl-3-phenylpropanoic acid hydrochloride. This experimentally determined relationship permitted assignment of the geometry of a number of β-lactam, carboxamido-1,3-butadiene, and amino acid products.

With a few exceptions, the principal mode of electrophilic (E^+) addition to cyclic and 1,3-disubstituted, straight-chain allenes has been *via* path a, while allene itself and monosubstituted allenes react predominantly *via* the vinyl carbonium (4) route (path b).[4] Attack by the nucleophile (N^-) on carbonium ions 2



and 4 complete the reaction to observed products 3 and 5, respectively.

Recently we reported that the stepwise 1,2-dipolar cycloaddition of chlorosulfonyl isocyante (CSI) to allenes [2,4-dimethyl-2,3-pentadiene (6a), 3-methyl-1,2-butadiene (6d), pentamethyleneallene (6e) and 1,2-cyclononadiene (6h)] proceeded *via* path a to produce initially, in the transition state, an allyl-type stabilized carbonium ion (7) leading ultimately to β-lactams (8, 9) and/or from the aqueous extract, 2-carboxamido-1,3-

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(2) Presented in part before the Organic Division, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p K76, and at the First International Congress of Heterocyclic Chemistry, the University of New Mexico, Albuquerque, N. M., June 12–15, 1967, Paper No. 76.

(3) Taken entirely from the Ph.D. Thesis of J. F. Kelly, 1969.

(4) For relevant references, including exceptions, *cf.* R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967); W. A. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1968); and two recent reviews of allene chemistry: A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, **33**, 1 (1964); H. Fischer in "Cumulenes," S. Patei, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1060–1083.