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Diels-Alder Reaction of "Anhydrochloral-urethane" with 1,3-Dienes[1]

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"Anhydrochloral-urethane" *N*-(2,2,2-trichloroethylidene)alkoxycarbonylamine (I), known since 1891,[2] was not actually synthesized until 1968 by Ulrich and his coworkers.[3] They gave good evidences of the reactivity of the C=N double bond in imine I toward the addition of nucleophiles.

The strongly electrophilic C=N double bond in some imines is successfully applied to the Diels-Alder reaction.[4] The enhanced electrophilicity and the simplicity of substituents prompted us to subject imine I ($R=C_2H_5$) to the Diels-Alder reaction as a dienophile affording the 2-ethoxycarbonyl-3-trichloromethyl-2-azabicyclo[2.2.1]heptenes (IIa, b) or 1-ethoxycarbonyl-2-tri-chloromethyl-1,2,3,6-tetrahydropyridines (III).

Reaction of I with cyclopentadiene in refluxing benzene for 3 hr gave two isomeric adducts in the ratio 2: 1 (90% combined yield). The 1 : 1 nature of these adducts was evidenced by elemental analyses and MS spectroscopy which gave a peak corresponding to the M^+-CCl_3 fragment ion as the base peak originated from the fragmentation β to the nitrogen atom, accompanied by a very weak molecular ion peak. The predominant crystalline adduct (IIa) was shown to possess an *exo* trichloromethyl group and the minor oily product (IIb) an *endo* trichloromethyl function, by NMR and IR spectroscopy. Especially noteworthy was the coupling constant between the proton α to the trichloromethyl group and the bridgehead proton. The value for IIa was 3.0 Hz, whereas that for IIb was nearly 0 Hz (Table 1). This difference is recognized in the elucidation of the sterochemistry of bicyclo[2.2.1]heptane ring systems.[5] It is further endorsed by the chemical shifts of the bridge methylene protons. Although both the methylene protons of IIb were degenerated at δ 1.66, the signals of those of IIa appeared at δ 1.45 and 2.74, indicating the anisotropic effect of the *exo* trichloromethyl on the nearer *syn* proton. The assignment of the configuration is also supported by IR spectra in CCl_4 solution, showing the carbonyl frequency of the urethane moiety of IIa at a higher wave number than that of IIb resulting from the decrease of overlap between the electrons of the carbonyl group and the lone-pair electrons of the nitrogen atom of IIa by a steric hindrance.

Kresze and Albrecht reported on the reaction of *N*-trichloroethylidene-*p*-toluenesulfonamide (IV) with

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[1] Partly presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April 1, 1971.

[2] R. Moscheles, *Ber.*, **24**, 1803 (1891); for the revised structure, see F. Feist, *ibid.*, **45**, 945 (1912).

[3] H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **33**, 2887 (1968).

[4] a) J.-P. Anselme, "The Chemistry of the Carbon-Nitrogen Bond", S. Patai, Ed., Interscience, New York, 1970, p. 299. b) A. B. Evnin, A. Lam, and J. Blyskal, *J. Org. Chem.*, **35**, 3097 (1970). c) D. Ben-Ishai and A. Warshawsky, *J. Heterocycl. Chem.*, **8**, 865 (1971) and their earlier works. d) D. vor der Brück, R. Bühler, and H. Plieninger, *Tetrahedron*, **28**, 791 (1972).

[5] For pertinent reference see M. Z. Haq, *J. Org. Chem.*, **37**, 3015 (1972).

Table 1. NMR chemical shifts,[a] multiplicities,[b] and coupling constants for II and III

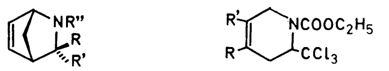
	H-3	H-4	H-5,6	H-1	H-7	*N*-Substituent
IIa	3.79(s)	3.54(bm)	6.52(cm)	4.81(m)	1.45(bd) 2.74(bd) (9.5 Hz)	1.30(t) 4.12(q) (7.0 Hz)
IIb	4.85(d)	3.80(bm)	6.47(m)	5.09(m)	1.66(t)	1.31(t) 4.18(q) (7.0 Hz)
IIc	4.04(s)	3.66(bm)	6.60(cm)	4.85(bm)	1.48(bd) 2.68(bd) (10.5 Hz)	2.38(s)(Me) 7.44(m)(ArH)
	H-3	H-6	H-2	=CH	$=CCH_3$	*N*-Substituent
IIIa	2.70(bs)	−4.2(AB)	5.22(m)	5.78(bs)	—	1.33(t) 4.22(q) (6.9 Hz)
IIIb	2.56(bs)	−4.0(AB)	5.25(m)	5.46(bs)	1.78(bs)	1.32(t) 4.21(q) (6.9 Hz)
IIIc	2.52(bs)	−3.8(AB)	5.14(m)	—	1.69(bs)	1.30(t) 4.18(q) (7.1 Hz)

a) δ values in CCl_4 (60 MHz). b) s, singlet, b, broad; d, doublet; m, multiplet; cm, complex multiplet; t, triplet; q, quartet; AB, AB quartet composed of broad lines (Only the central position is shown in δ values).

cyclopentadiene to give an adduct of mp 134 °C in 93% yield,[6] but no mention seems to have been made about its stereochemistry. On reexamining the reaction we confirmed that the configuration of the adduct IIc is in the same situation as that of our predominant adduct IIa by comparison of their NMR spectra. Both showed similar patterns of the protons in the azabicyclo[2.2.1]heptene rings.

$CCl_3CH=NCOOR$

I



IIa: $R=CCl_3$, $R'=H$, $R''=COOC_2H_5$

b: $R=H$, $R'=CCl_3$, $R''=COOC_2H_5$

c: $R=CCl_3$, $R'=H$, $R''=SO_2C_6H_4CH_3$-*p*

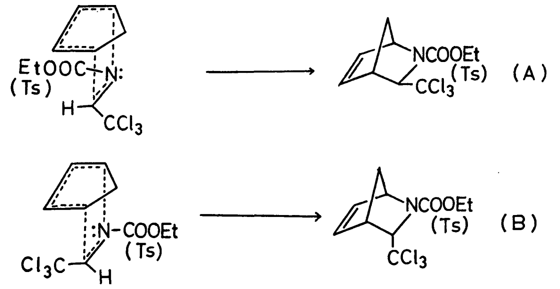
IIIa: $R=R'=H$

b: $R=CH_3$, $R=H'$

c: $R=R'=CH_3$

Formula.

At first glance, the *exo* orientation of the trichloromethyl group in the exclusive or major adduct seems inconsistent with the so-called *endo* addition rule.[7] However, the results are well explained on the basis of the rule of maximum accumulation of double bonds as follows (Scheme 1). When dienophiles I and IV are assumed to have *anti* configuration[8] at the transition state of the reaction, course A is more favorable than B, since not the trichloromethyl group but the conjugated ethoxycarbonyl or *p*-toluenesulfonyl group should play a dominant role in the maximum overlapping of unsaturation. Consequently, the major or exclusive product has the trichloromethyl group in the *exo* arrangement. The reason for IV exclusively giving the *exo* adduct but I the *exo*- as well as *endo*-adduct may be ascribed to the stronger directive effect of the sulfonyl group, since the Diels-Alder reaction of *trans*-1-benzoyl-2-benzenesulfonylethylene and cyclopentadiene has been reported[9] to give the *endo* benzenesulfonyl adduct and the *endo* benzoyl adduct in the ratio 3: 1.



Scheme 1.

Heating benzene solutions of I and butadiene, isoprene, and 2,3-dimethylbutadiene in a pressure bottle at 100—120 °C gave 1-ethoxycarbonyl-2-trichloromethyl-1,2,3,6-tetrahydropyridines (IIIa—c) in 55, 75, and 78% yield, respectively. The adduct of isoprene was a single compound and tentatively assigned to IIIb, because the chemical shift of the protons of C_3 was nearer that of IIIc than IIIa; this assignment and the regiospecificity are consistent with the result in an analogous reaction.[10]

Experimental[11]

Reaction of I with Cyclopentadiene. Refluxing a benzene (25 ml) solution of freshly prepared I (5.00 g) and cyclopentadiene (2.5 g) for 3 hr gave an oily mixture after evaporation. This was chromatographed over 80 g of alumina with benzene as an eluent.

The faster moving zone gave, after removal of the solvent, 3.85 g (59%) of oily IIa; bp 136—138 °C/4 mmHg, $n_D^{23.5°}$

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6) G. Kresze and R. Albrecht, *Chem. Ber.*, **97**, 490 (1964).

7) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970. p. 145,

8) Although *syn-anti* isomerism in I and IV has not been established, the distribution of products may be safely discussed on the *anti* configuration which is stable in the transition state; for *syn-anti* isomerism in imines, see a) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971); b) R. M. Moriarty, C.-L. Yeh, K. C. Ramey, and P. W. Whitehurst, *ibid.*, **92**, 6350 (1970); and the references cited therein.

9) J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

10) R. Albrecht and G. Kresze, *Chem. Ber.*, **98**, 1431 (1965).

11) MS spectra were obtained with an ionization potential of 70 eV. We are grateful to Dr. Simpei Kojima for permission to use the NMR spectrometer. I and IIc, prepared by the reported procedures, had spectral properties in agreement with those in literature,

1.5159. IR (CCl_4): 1730, 1270 cm^{-1}. MS: *m/e* 283 (small, M^+), 166 (100%, M^+-CCl_3), 138 (16), 94 (46), 67 (30), 66 (30), 56 (45%), M: M+2: M+4: M+6=100: 98: 32: 4. Found: C, 42.15; H, 4.24; N, 4.65%. Calcd for $C_{10}H_{12}Cl_3NO_2$: C, 42.20; H, 4.25; N, 4.92%.

From the slower moving zone, 2.01 g (30%) of IIb was obtained as colorless crystals, mp 47.5—48.0 °C. IR (CCl_4): 1708, 1270 cm^{-1}. MS: *m/e* 283 (small, M^+), 166 (M^+-CCl_3, 110%), 138 (18), 94 (36), 67 (33), 66 (40), 56 (51%), M: M+2: M+4: M+6=100: 100: 32: 4. Found: C, 42.31; H, 4.21; N, 4.71%. Calcd for $C_{10}H_{12}Cl_3NO_2$: C, 42.20; H, 4.25; N, 4.92%.

Reactions of I with Other 1,3-Dienes. A solution of 4 g of I and a large excess of 1,3-dienes in 10 ml of benzene was heated in a pressure bottle. Removal of the solvent and vacuum distillation gave oily products. Analytically pure samples were obtained by column chromatography (alumina, benzene).

IIIa was obtained from I and butadiene (100 hr at 115 °C, 55%); bp 126—127 °C/3 mmHg, $n_D^{24.0°}$ 1.5114. IR (neat): 1720 cm^{-1}. MS: *m/e* 271 (M^+, small), 154 (M^+-CCl_3, 100%), 126 (16), 108 (14), 82 (33), 80 (26), 54 (9%), M: M+2: M+4: M+6=100: 100: 31: 4. Found: C, 39.74; H, 4.51; N, 4.90%. Calcd for $C_9H_{12}Cl_3NO_2$: C, 39.66; H, 4.44; N, 5.14%.

IIIb was obtained from I and isoprene (80 hr at 100 °C, 75%); bp 125—127 °C/3 mmHg, $n_D^{25.0°}$ 1.5062. IR (neat): 1718 cm^{-1}. MS: *m/e* 285 (M^+, small), 168 (100%, M^+-CCl_3), 140 (15), 122 (10), 96 (25), 94 (19), 79 (10), 68 (10), 56 (19%), M: M+2: M+4: M+6=100: 100: 32: 4. Found: C, 42.10; H, 4.96; N, 4.80%. Calcd for $C_{10}H_{14}Cl_3NO_2$: C, 41.91; H, 4.92; N, 4.89%.

IIIc was obtained from I and 2,3-dimethylbutadiene (48 hr at 100 °C, 78%); bp 126—130 °C/3 mmHg, $n_D^{20.8°}$ 1.5074. IR (neat): 1720 cm^{-1}. MS: *m/e* 299 (M^+, 7%), 264 (13), 182 (M^+-CCl_3, 100), 154 (27), 136 (14), 110 (31), 108 (36), 93 (38), 67 (15), 56 (18%), M: M+2: M+4: M+6=100: 98: 31: 4.

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